Chapter 18
Thermodynamics and Equilibrium

Overview of the Chapter
- Look at equilibrium from the perspective of thermodynamics
  - energy considerations in chemical reactions
  - introduce 2 new thermodynamic quantities, entropy ($\Delta S$) and Gibbs free energy ($\Delta G$)
- What are the factors that determine where a reaction reaches equilibrium?
- What fundamental properties determine the direction in which a reaction will proceed?

Spontaneous Processes
- a spontaneous process is one that proceeds on its own without any external intervention
- the reverse of a spontaneous process is always non-spontaneous; requires external intervention
- a spontaneous process will always move a system toward equilibrium

examples:
- expansion of a gas from region of higher $P$ to region of lower $P$:
  - Stopcock closed
  - Stopcock open

- a boulder rolling down a hill:
examples:

chemical reactions and phase changes are spontaneous in one direction and non-spontaneous in the reverse direction

\[ 2 \text{H}_2 (g) + \text{O}_2 (g) \rightarrow 2 \text{H}_2\text{O} (l) \]
\[ \text{NaCl} (s) \rightarrow \text{Na}^+ (aq) + \text{Cl}^- (aq) \]
\[ \text{H}_2\text{O} (s) \rightarrow \text{H}_2\text{O} (l) \]

Kinetics vs. Thermodynamics

- be careful not to confuse a “fast” reaction and a “spontaneous” reaction
- kinetics tells us about:
  - rates of reaction
  - path from reactants to products
  - activation energy
- thermodynamics tells us about:
  - relative energy levels of reactants and products
  - absorption or release of heat during the change

Enthalpy, Entropy and Spontaneous Processes

What do spontaneous processes have in common?

- not all are exothermic:
  \[ \text{H}_2\text{O} (s) \rightarrow \text{H}_2\text{O} (l); \quad \Delta H = + 6.01 \text{ kJ} \]
  \[ \text{NaCl} (s) \rightarrow \text{Na}^+ (aq) + \text{Cl}^- (aq); \quad \Delta H = + 3.88 \text{ kJ} \]
- there must be another consideration besides \( \Delta H \)
- all spontaneous processes have in common a tendency toward increasing randomness or disorder
  thermodynamic quantity entropy, \( S \)
  \[ \Delta S = S_{\text{final}} - S_{\text{initial}} \]
  when disorder increases: \( S_{\text{final}} > S_{\text{initial}} \); \( \Delta S \) is +
  when disorder decreases: \( S_{\text{final}} < S_{\text{initial}} \); \( \Delta S \) is –

Factors that Influence Entropy (Disorder)

- physical states of reactants and products
  \( S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}} \)
- number of particles
  as \( n \) increases, disorder increases
- volume occupied by gas phase sample
  as \( V \) increases, “positional” entropy increases; more positions in space that can be occupied by particle
- temperature of gas phase sample
  as \( T \) increases, entropy increases
  increase in kinetic energy & thermal motion
Statistics and Probability

- there are more ways to have a disordered state than an ordered state
- systems tend naturally toward a state of greater disorder because disordered states are more probable than ordered states

example:
Consider 5 quarters tossed randomly in a box. What are the possible head:tail (H:T) configurations?

<table>
<thead>
<tr>
<th>H</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>

- each of these is called a macrostate;
  here there are 6 possible macrostates

- now consider the specific, possible quarter-by-quarter combinations

- each of these specific combinations is called a microstate;
  here there are 32 \(2^5\) possible microstates

the specific quarter by quarter H:T microstates possible:

<table>
<thead>
<tr>
<th>H</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHHHH (1 microstate)</td>
<td>TTTTT (1 microstate)</td>
</tr>
<tr>
<td>THHHH</td>
<td>HHHHH</td>
</tr>
<tr>
<td>THHHH</td>
<td>HTHHH</td>
</tr>
<tr>
<td>HHTHH (5 microstates)</td>
<td>TTTHT (5 microstates)</td>
</tr>
<tr>
<td>HHHTH</td>
<td>THTHT</td>
</tr>
<tr>
<td>HHTHT</td>
<td>TTHTT</td>
</tr>
<tr>
<td>TTTHH</td>
<td>HHTHT</td>
</tr>
<tr>
<td>TTHHH</td>
<td>HHTTT</td>
</tr>
<tr>
<td>THTHH</td>
<td>HTHTT</td>
</tr>
<tr>
<td>HTTHH (10 microstates)</td>
<td>THTHT (10 microstates)</td>
</tr>
<tr>
<td>HHTTH</td>
<td>HTTHT</td>
</tr>
<tr>
<td>HTHHT</td>
<td>THTTH</td>
</tr>
<tr>
<td>HHTHT</td>
<td>TTHTH</td>
</tr>
<tr>
<td>HHHHT</td>
<td>THTHH</td>
</tr>
<tr>
<td>HHTTT</td>
<td>TTHHT</td>
</tr>
<tr>
<td>HHTTH</td>
<td>THTTH</td>
</tr>
<tr>
<td>HHTHT</td>
<td>TTTTH</td>
</tr>
<tr>
<td>HHHHT</td>
<td>TTTTT</td>
</tr>
</tbody>
</table>

- consider the probabilities of ending up with more or less order in this 5 quarter system:

  What is the probability that you will get a completely ordered state - either 5 H or 5 T?
  2 out of 32, or 6.25%

  What is the probability that you will get a disordered state - either 3 H : 2 T, or 2 H : 3 T?
  20 out of 32, or 62.5%

- notice that the most probable states correspond to the greatest disorder, or highest entropy
example:

Predict (if possible) the sign of $\Delta S$ for the following changes:

\[
\text{CO}_2 (s) \rightarrow \text{CO}_2 (g)
\]
\[
\text{CaSO}_4 (s) \rightarrow \text{CaO} (s) + \text{SO}_3 (g)
\]
\[
\text{N}_2 (g) + 3 \text{H}_2 (g) \rightarrow 2 \text{NH}_3 (g)
\]

A 1.0 mol sample of $\text{N}_2 (g)$ is subjected to an increase in temperature from 100 K to 250 K, and as a result expands to occupy 4 x its initial volume.

The 2nd Law of Thermodynamics

- The entropy of the Universe is increasing.
- Processes will proceed spontaneously in the direction that increases the entropy of the Universe.

\[
\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}
\]

- if $\Delta S_{\text{univ}} > 0$ spontaneous process
- if $\Delta S_{\text{univ}} < 0$ non-spontaneous process
- if $\Delta S_{\text{univ}} = 0$ equilibrium

Calculating $\Delta S_{\text{sys}}, \Delta S_{\text{surr}},$ and $\Delta S_{\text{univ}}$

- $\Delta S_{\text{sys}}$ can be calculated using *standard molar entropy values* ($S^\circ$)
  - tabulated in Appendix C of your text
  - units J/K•mol
  - note: $S^\circ \neq 0$ for elements

\[
\Delta S_{\text{sys}} = \sum nS^\circ_{\text{products}} - \sum nS^\circ_{\text{reactants}}
\]

example:

Calculate $\Delta S^\circ$ for the following reaction:

\[
\text{N}_2\text{O}_4 (g) \rightarrow 2 \text{NO}_2 (g)
\]

For $\text{N}_2\text{O}_4$, $S^\circ = 304.2 \text{ J/K}•\text{mol}$; for $\text{NO}_2$, $S^\circ = 240.0 \text{ J/K}•\text{mol}$. 
Calculating $\Delta S_{\text{sys}}, \Delta S_{\text{surr}},$ and $\Delta S_{\text{univ}}$

- For a reaction at constant $P$, $\sum S_{\text{surr}}$ is directly proportional and opposite in sign to $\Delta H$, and inversely proportional to $T$.

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

example:

Consider the following reaction:

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

Is this reaction spontaneous at 25°C?

Calculate $\Delta S^\circ_{\text{sys}}$ using $S^\circ$ values.
Calculate $\Delta S^\circ_{\text{surr}}$ using $\Delta H^\circ_f$ values and $T$.
Calculate $\Delta S^\circ_{\text{univ}}$.

some data:

<table>
<thead>
<tr>
<th>$S^\circ$ (J/K•mol)</th>
<th>$\Delta H^\circ_f$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe (s): 27.3</td>
<td>0</td>
</tr>
<tr>
<td>O$_2$ (g): 205.0</td>
<td>0</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ (s): 87.4</td>
<td>-824.2</td>
</tr>
</tbody>
</table>

A System at Equilibrium?

What are the relationships between $\Delta S_{\text{sys}}, \Delta S_{\text{surr}},$ and $\Delta S_{\text{univ}}$ when a system is at equilibrium?

$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$

at equilibrium, $\Delta S_{\text{univ}} = 0$

$\therefore \Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$

example:

Diethyl ether, (C$_2$H$_5$)$_2$O, is a solvent and anesthetic. The heat of vaporization of diethyl ether at its boiling point ($35.6^\circ$C) is 26.7 kJ/mol.

Determine the change in entropy when 1.34 mol diethyl ether vaporizes at its boiling point.
Gibbs Free Energy, $\Delta G$

$G = H - TS$

- for a process at constant $T$ and $P$:
  
  $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$

- How does this relate to spontaneity?

$\Delta G$ and Spontaneous Processes

- a $+$ value for $\Delta S_{univ}$ indicates spontaneous change

- a $-$ value for $\Delta G_{sys}$ indicates spontaneous change

For a reaction at constant $T$ and $P$:

- if $\Delta G_{sys} < 0$, spontaneous process
- if $\Delta G_{sys} > 0$, non-spontaneous process
- if $\Delta G_{sys} = 0$, equilibrium

Temperature Dependence of Spontaneous Change:

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

- $\Delta H$ and $\Delta S$ both play a role in the spontaneity of a process, but $T$ may be the weighting factor.

<table>
<thead>
<tr>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
<th>$\Delta G^\circ$</th>
<th>Description*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-$</td>
<td>$+$</td>
<td>$-$</td>
<td>Spontaneous at all $T$</td>
</tr>
<tr>
<td>$+$</td>
<td>$-$</td>
<td>$+$</td>
<td>Nonspecial at all $T$</td>
</tr>
<tr>
<td>$-$</td>
<td>$-$</td>
<td>$+$ or $-$</td>
<td>Spontaneous at low $T$; nonspecial at high $T$</td>
</tr>
<tr>
<td>$+$</td>
<td>$+$</td>
<td>$+$ or $-$</td>
<td>Nonspecial at low $T$; spontaneous at high $T$</td>
</tr>
</tbody>
</table>

- the crossover temperature is the $T$ above or below which the reaction becomes spontaneous

example:

Consider the reaction:

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

For this reaction $\Delta H^\circ = +98.8$ kJ, and $\Delta S^\circ = +141.5$ J/K.

Is this reaction spontaneous at 25°C?

If not, at what temperature does the reaction become spontaneous?
Calculating $\Delta G^\circ$ for Reactions

- use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- use Hess's Law of Heat Summation approach
  \textit{review Chapter 6.3, problems 6.51 - 6.57}
- use $\Delta G^\circ_f$ values
  free energy change for the formation of 1 mol of a
  substance in its standard state from its constituent
  elements in their standard states
  $\Delta G^\circ_f$ of element in its most stable form = 0
  units kJ/mol
  tabulated in Appendix C
  $\Delta G^\circ = \sum n\Delta G^\circ_f (\text{products}) - \sum n\Delta G^\circ_f (\text{reactants})$

example:
Calculate $\Delta G^\circ$ for the reaction using the given $\Delta G^\circ_f$
data:

\[
4 \text{NH}_3 (g) + 5 \text{O}_2 (g) \rightarrow 4 \text{NO} (g) + 6 \text{H}_2\text{O} (l)
\]

$\Delta G^\circ_f (kJ/mol)$:
- $\text{NH}_3 (g) = -16.5$
- $\text{NO} (g) = +86.6$
- $\text{O}_2 (g) = 0$
- $\text{H}_2\text{O} (l) = -273.2$

\text{answer: } -1226.8 \text{ kJ}$

Free Energy and Reaction Composition

- at non-standard conditions:
  $\Delta G = \Delta G^\circ + RT \ln Q$

- $\Delta G$ and $Q$ are related because both predict the
direction of reaction

example:
Calculate $\Delta G$ for the following reaction at 25°C
when $P_{N_2} = 1.0$ atm, $P_{H_2} = 3.0$ atm, and
$P_{NH_3} = 0.020$ atm:

\[
\text{N}_2 (g) + 3 \text{H}_2 (g) \rightleftharpoons 2 \text{NH}_3 (g); \quad \Delta G^\circ = -33.0 \text{ kJ/mol}
\]

Free Energy and Equilibrium

- $\Delta G$ and $Q$ are related
  both depend on composition
  both can be used to predict the direction of reaction
- consider how $\Delta G$ changes as a system moves toward
equilibrium
Free Energy and Equilibrium

consider 2 extremes:

- if [reactants] large & [products] small
  
  \[ Q << 1 \]
  \[ RT\ln Q < 0 \]
  \[ \Delta G < 0 \]

  reaction spontaneous in the forward direction

- if [products] large & [reactants] small
  
  \[ Q >> 1 \]
  \[ RT\ln Q > 0 \]
  \[ \Delta G > 0 \]

  reaction spontaneous in the reverse direction

Free Energy and Equilibrium

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

at equilibrium: \( \Delta G = 0 \)

\[ Q = K \]

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

example:

Determine the value of \( K \) at 25°C for the following rxn:

\[ \text{CO (g)} + 2 \text{H}_2 (g) \rightleftharpoons \text{CH}_3\text{OH (g)} \]

\( \Delta G^\circ_f = -137.2 \text{ kJ/mol for CO (g)}; \ -161.9 \text{ kJ/mol for CH}_3\text{OH (g)} \)

Free Energy and Equilibrium

- somewhere in between the 2 extremes:
  
  the system reaches equilibrium
  
  goes through an energy minimum

- equilibrium composition corresponds to lowest free energy

- moving toward equilibrium is spontaneous

- moving away from equilibrium is non-spontaneous

- at equilibrium, \( \Delta G = 0 \)

Temperature Dependence of K

- \( K \) is dependent on \( T \) for a given rxn at constant \( P \):

  \[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{and} \quad \Delta G^\circ = -RT\ln K \]

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

  further:

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