Chapt 2: Basics

- Thermodynamics
  - Will tell you
    - which reactions are favorable or “Possible”
    - composition of systems at equilibrium
  - Won’t tell you
    - how quickly the reactions proceed
- good for systems with constant P & T
  - Air: 1.0 atm at sea level
  - Water: 1.0 atm for each additional 10.7 m of water
  - Earth: wt of overlying rock and soil
- Governing property @ const. T&P is the Gibbs Free Energy
  - for constant T&V, it is the Helmholtz Free Energy

Sets limits
Thermodynamics: Examples

- Removal of P from wastewater by Alum
  - is it possible?  Yes
  - What is best pH?  Yes
  - What is the final P concentration?  Yes
  - How much is removed in treatment system?  No

- Ammonia stripping
  - best pH?

- Acid rain
  - pH of “pure” rainwater?

Open & Closed Systems

- Closed Systems
  - No significant flux of material into or out of system
  - Like an isolated beaker of water
  - Steady state condition is the true chemical equilibrium

- Open systems
  - Mass movement across system boundary from or to outside world
  - More realistic, but more complicated
  - Steady state condition may not be true chemical equilibrium, due to continuous perturbation from outside
Laws of Thermodynamics

1st Law
- Conservation of energy
  - best you can hope for is "break even"
  - \[ dE = dq - dw \]

2nd Law
- Entropy of the universe tends to increase
  - you can't even "break even"
  - \[ dS_{sys} > \frac{dq}{T}, \text{ for irreversible processes} \]
  - \[ dS_{univ} = dS_{sys} + dS_{surr} \geq 0 \]

3rd Law
- Entropy is zero for a perfect crystal at absolute zero

Combining 1st & 2nd Laws

- Internal Energy Change for reversible processes
  - \[ dE = dq - dw \]
  - \[ dE = TdS_{sys} - dw \]
  - \[ dE = TdS_{sys} - pdV \]

- But for a system not at equilibrium that is undergoing an irreversible process, entropy must increase beyond dq/T
  - \[ dE < TdS_{sys} - pdV \]
  - \[ dE - TdS_{sys} + pdV < 0 \]
  - \[ dS_{sys} = dS + dq / T \]

- And taking into account the entropy increase, dS, we can maintain the equality
  - \[ dE = TdS_{sys} - TdS - pdV \]
Enthalpy

- A fundamental thermodynamic variable
- Enthalpy change is equal to heat of reaction (for systems at constant pressure)
  - $\Delta H < 0$, heat is given off exothermic
  - $\Delta H > 0$, heat is absorbed endothermic
- $\Delta H$ can be calculated from standard enthalpies of formation ($\Delta H^o_f$)
  - available in many texts
    - e.g., Snoeyink & Jenkins, Table 3-1

$$\Delta H^o = \sum v_i \Delta H^o_f$$

Example

- Evaporation of water
  - $\Delta H^o = \sum v_i \Delta H^o_f$
  - $\Delta H^o = (1 \text{ mole})(-57.80 \text{ kcal/mole}) + (-1 \text{ mole})(-68.32 \text{ kcal/mole})$
  - $= +10.52 \text{ kcal}$

- $\Delta H > 0$, heat is absorbed endothermic
  - However, this does not tell us if the reaction is favorable, or proceeds spontaneously
    - to answer this we need to know the entropy change
### Thermodynamic Constants for Species of Importance in Water Chemistry (Table 3-1 from Snoeyink & Jenkins) Part I

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H_f$</th>
<th>$\Delta G_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{+2}$(aq)</td>
<td>-129.77</td>
<td>-132.18</td>
</tr>
<tr>
<td>CaCO$_3$(s), calcite</td>
<td>-288.45</td>
<td>-269.78</td>
</tr>
<tr>
<td>CaO (s)</td>
<td>-151.9</td>
<td>-144.4</td>
</tr>
<tr>
<td>C(s), graphite</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO$_3$(g)</td>
<td>-94.05</td>
<td>-94.26</td>
</tr>
<tr>
<td>CO$_2$(aq)</td>
<td>-98.69</td>
<td>-92.31</td>
</tr>
<tr>
<td>CH$_4$(g)</td>
<td>-17.889</td>
<td>-12.140</td>
</tr>
<tr>
<td>H$_2$CO$_3$(aq)</td>
<td>-167.0</td>
<td>-149.00</td>
</tr>
<tr>
<td>HCO$_3$- (aq)</td>
<td>-165.18</td>
<td>-140.31</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H_f$</th>
<th>$\Delta G_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_3$- (aq)</td>
<td>-161.63</td>
<td>-126.22</td>
</tr>
<tr>
<td>CH$_3$COO$^-$(aq), acetate</td>
<td>-116.84</td>
<td>-49.0</td>
</tr>
<tr>
<td>H$^+$ (aq)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H$_2$O (g)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO$_2$(aq)</td>
<td>-21.0</td>
<td>-20.30</td>
</tr>
<tr>
<td>Fe$^{2+}$ (aq)</td>
<td>-11.4</td>
<td>-2.52</td>
</tr>
<tr>
<td>Fe$^+$ (aq)</td>
<td>-21.0</td>
<td>-11.4</td>
</tr>
<tr>
<td>Fe(OH)$_3$ (s)</td>
<td>-197.0</td>
<td>-166.0</td>
</tr>
<tr>
<td>Mn$^{2+}$ (aq)</td>
<td>-53.3</td>
<td>-54.4</td>
</tr>
<tr>
<td>MnO$_2$ (s)</td>
<td>-124.2</td>
<td>-111.1</td>
</tr>
</tbody>
</table>

### Thermodynamic Constants for Species of Importance in Water Chemistry (Table 3-1 from Snoeyink & Jenkins) Part II

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H_f$</th>
<th>$\Delta G_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{+2}$ (aq)</td>
<td>-120.41</td>
<td>-138.99</td>
</tr>
<tr>
<td>Mg(OH)$_2$ (s)</td>
<td>-221.00</td>
<td>-199.27</td>
</tr>
<tr>
<td>NO$_3$- (aq)</td>
<td>-49.372</td>
<td>-66.43</td>
</tr>
<tr>
<td>NH$_3$ (g)</td>
<td>-11.04</td>
<td>-3.96</td>
</tr>
<tr>
<td>NH$_4$+ (aq)</td>
<td>-19.32</td>
<td>-6.37</td>
</tr>
<tr>
<td>NH$_3$ (aq)</td>
<td>-31.74</td>
<td>-9.00</td>
</tr>
<tr>
<td>HNO$_3$ (aq)</td>
<td>-49.372</td>
<td>-26.41</td>
</tr>
<tr>
<td>O$_2$ (aq)</td>
<td>-3.9</td>
<td>3.93</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H_f$</th>
<th>$\Delta G_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$ (g)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OH$^-$ (aq)</td>
<td>-54.957</td>
<td>-37.595</td>
</tr>
<tr>
<td>H$_2$O (g)</td>
<td>-57.7979</td>
<td>-54.6357</td>
</tr>
<tr>
<td>H$_2$O (l)</td>
<td>-68.3174</td>
<td>-56.690</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>-216.90</td>
<td>-177.34</td>
</tr>
<tr>
<td>HS$^-$ (aq)</td>
<td>-4.22</td>
<td>3.01</td>
</tr>
<tr>
<td>H$_2$S(g)</td>
<td>-4.815</td>
<td>-7.892</td>
</tr>
<tr>
<td>H$_2$S(aq)</td>
<td>-9.4</td>
<td>-6.54</td>
</tr>
</tbody>
</table>
Entropy

- A measure of a system’s randomness
- remove the partition and randomness increases
  - 2nd law of Thermo.
- Spontaneous in isolated system
  - Like water running downhill
  - Or hot objects heating colder ones

\[ \Delta S^o = \sum V_i \Delta S_f^o \]

Gibbs Free Energy

- Combines enthalpy and entropy
- 1st and 2nd laws of thermodynamics
- Determines whether a reaction is favorable or spontaneous
- Practical form is based on an arbitrary datum
  - the pure and most stable form of each element at standard state

\[ \Delta G^o = \Delta H^o - T \Delta S^o \]
Standard State

- Standard State
  - Conditions:
    - Unit activity (a=1)
    - Rarely encountered in practice; but easier to base calculations on
  - State variables: $\Delta G^0$, $\mu^0$

- Non-standard State
  - Conditions:
    - Non-unit activity, often quite low
    - This is the “real world”
  - State Variables: $\Delta G$, $\mu$

Solving problems with $G$

Recall, at any T & P: $\Delta G^0 = \sum \nu_i \mu_i^0$

- $\Delta G$ can be calculated at 25°C from standard gibbs free energies of formation ($G^0_f$)
  - These are essentially $\Delta G$'s for the formation of chemical substances from the most stable forms of their constituent elements
  - available in many texts
    - e.g., Stumm & Morgan, Appendix 3
    - e.g., Benjamin, Table 2.1
    - e.g., Snoeyink & Jenkins, Table 3.1

Conversion: 1 kcal = 4.184 kJ

But for STP, we use:

$\Delta G^0 = \sum \nu_i G^0_f$
Ammonia Problem (1/7)

- Determine $\Delta G^o$ for dissolution of ammonia in water at 25°C

$$NH_3(g) \leftrightarrow NH_3(aq)$$

- Based on example 2.5 in text
- Two approaches
  - A. Determine $\Delta G^o$ directly from individual $G^o_f$'s
    - The easiest way
  - B. Determine $\Delta G^o$ from $\Delta H^o$ and $\Delta S^o$

Ammonia Problem (2/7)

- A. Determine $\Delta G^o$ directly from individual $G^o_f$'s
  - Get thermodynamic data
    - from Appendix A (Benjamin) or Appendix 3 (S&M)
  - Expand equation and substitute data

$$\Delta G^o = \sum v_i G^o_f$$

$$\Delta G^o = V_{NH_3(g)} G^o_{f-NH_3(g)} + V_{NH_3(aq)} G^o_{f-NH_3(aq)}$$

$$= (-1)(-16.48) + (1)(-26.57)$$

$$= -10.09$$

Units are kJ/mole

<table>
<thead>
<tr>
<th>Species</th>
<th>Formation from the Elements</th>
<th>$G^o_f$ (kJ mol$^{-1}$)</th>
<th>$H^o_f$ (kJ mol$^{-1}$)</th>
<th>$S^o$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$(g)</td>
<td>-16.48</td>
<td>-46.1</td>
<td>192</td>
<td>NBS</td>
<td></td>
</tr>
<tr>
<td>NH$_3$(aq)</td>
<td>-26.57</td>
<td>-80.29</td>
<td>111</td>
<td>NBS</td>
<td></td>
</tr>
<tr>
<td>NH$_4^+$ (aq)</td>
<td>-79.37</td>
<td>-132.5</td>
<td>113.4</td>
<td>NBS</td>
<td></td>
</tr>
</tbody>
</table>
Ammonia Problem (3/7)

B. Determine $\Delta G^o$ from $\Delta H^o$ and $\Delta S^o$
- Get thermodynamic data from Appendix A (or 3)
- Expand equations and substitute data

$$\Delta H^o = \sum v_i \Delta H^o_f$$

$$\Delta S^o = \sum v_i S^o$$

$$\Delta H^o = \nu_{NH_3(g)}^{\Delta H_f^{\text{NH}_3(g)}} + \nu_{NH_3(aq)}^{\Delta H_f^{\text{NH}_3(aq)}}$$

$$= (-1)(-46.1) + (1)(-80.29)$$

$$= -34.19 \text{ Units are kJ/mole}$$

$$\Delta S^o = \nu_{NH_3(g)}^{S^o} + \nu_{NH_3(aq)}^{S^o}$$

$$= (-1)(192) + (1)(111)$$

$$= -81 \text{ Units are J/mole/}^o\text{K}$$

Ammonia Problem (4/7)

- Now combine and solve for $\Delta G^o$

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

$$= (-34.19) - (273.16 + 25)(-81)(\frac{1kJ}{1000J})$$

$$= -10.04 \text{ Units are kJ/mole}$$

- Conclusion: reaction is spontaneous since $\Delta G^o < 0$
- Lingering question: what actually happens when we’re not at standard state conditions (i.e., when activity isn’t equal to one)?
Chemical Potential

- Like a Gibbs Free Energy normalized per mole

- a function of activity and temperature

\[ \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P} \]

\[ \mu_i = \mu_i^o + RT \ln a_i \]

kJ/mole

kJ

Standard state (unit activity)

This term corrects for the fact that we’re not at unit activity

Example

- Activities in concentrated NaCl solution
  - S&M: Example 2.3 (pg 40)
General Condition

- And relating to the change in G for complete conversion to products

\[ \Delta G = \sum v_i \mu_i \]
\[ = \sum v_i (\mu_i^o + RT \ln a_i) \]
\[ = \sum v_i \mu_i^o + RT \sum v_i \ln a_i \]

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

where \[ Q = \frac{a_c a_D}{a_a a_B} \]

For the reaction: \[ aA + bB \leftrightarrow cC + dD \]

Ammonia problem (5/7)

- Now lets see what the \( \Delta G \) is for the following non-standard conditions
  - \([\text{NH}_3(aq)] = 10^{-3} \text{ M}\)
  - \(p_{\text{NH}_3} = 10^{-4} \text{ atm}\)
  - Now we need to determine Q
  - Recall the reaction: \( \text{NH}_3(g) \leftrightarrow \text{NH}_3(aq) \)
  - So:

\[ Q = \frac{a_{\text{NH}_3(aq)}}{a_{\text{NH}_3(g)}} \approx \frac{10^{-3}}{10^{-4}} = 10 \]
Ammonia problem (6/7)

- Now substitute back into the equation for $\Delta G$

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

\[
= -10.04 + (0.008314)(273.16 + 25) \ln(10)
\]

\[
= -4.33 \quad \text{Units are kJ/mole}
\]

- Conclusion: the reaction is still spontaneous at these non-standard concentrations
  - i.e., the reaction will proceed toward the right
- Another lingering question: how far to the right will it proceed before it reaches equilibrium and stops?
  - To answer this we need to determine “$K$”

Equilibrium Quotients

- at Equilibrium $\Delta G = 0$, so:
  - and:

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

\[
= -2.303RT \log K
\]

- or:

\[
\log K = -\frac{\Delta G^\circ}{2.303RT}
\]

Where $K$ is defined as the quotient (Q) at equilibrium and is generally referred to as the “equilibrium constant”

\[
K = \frac{a_c a_d}{a_a a_b}, \text{ at equilibrium}
\]
Ammonia problem (7/7)

To determine the equilibrium position of ammonia dissolution, we need the equilibrium constant, $K$

$$\log K = -\frac{\Delta G^o}{2.303RT}$$

$$= -\frac{-10.04}{2.303(0.008314)(273.16 + 25)}$$

$$= 1.76$$

So as we approach equilibrium, $Q$ will approach the value of $K$, which is 57.4

$$Q = \frac{a_{\text{H}_2\text{O}(aq)}}{a_{\text{H}_2\text{O}(g)}} \approx \frac{10^{-3}}{10^{-4}} = 10$$

Quotients (cont.)

more generally, for non-equilibrium conditions, we can combine:

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

$$= -RT \ln K + RT \ln Q$$

$$= RT \ln \left( \frac{Q}{K} \right)$$

$$\Delta G = 2.303RT \log \left( \frac{Q}{K} \right)$$

and if,

- $\Delta G < 0$, $(Q/K) < 1$, and equilibrium lies to the right
- $\Delta G > 0$, $(Q/K) > 1$, and equilibrium lies to the left
- $\Delta G = 0$, $(Q/K) = 1$, and system is at equilibrium
Gibbs Energy of a System

- G changes as reaction progresses due to changing concentrations.
- G reaches a minimum at the point of equilibrium.

The $G_f^0$ Convention

- Since the $G_f^0$ values are essentially $\Delta G$'s for the formation of chemical substances from the "most stable" (reference) forms of their constituent elements.
  - The $G_f^0$ values for those most stable elemental forms are zero, by definition.
- Examples:
  - Zero-valent, Metallic Ag, Al, Fe, Mn, Pb, Zn
  - graphite-C, white-P, rhombic-S
  - diatomic $H_2$, $I_2$, $N_2$, $O_2$
Simple examples

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ \text{H}_2(\text{g}) + \text{S}(\text{s}) = \text{H}_2\text{S}(\text{aq})$</td>
<td>-27.87</td>
</tr>
<tr>
<td>$ \text{H}_2(\text{g}) + \text{S}(\text{s}) = \text{H}_2\text{S}(\text{g})$</td>
<td>-33.56</td>
</tr>
<tr>
<td>$ \text{O}_2(\text{g}) + \text{S}(\text{s}) = \text{SO}_2(\text{g})$</td>
<td>-300.2</td>
</tr>
<tr>
<td>$ \text{Hg}(\text{l}) + \text{S}(\text{s}) = \text{HgS}(\text{s})$</td>
<td>-43.3</td>
</tr>
<tr>
<td>$ \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{l})$</td>
<td>-237.18</td>
</tr>
<tr>
<td>$ \text{O}_2(\text{g}) = \text{O}_2(\text{aq})$</td>
<td>16.32</td>
</tr>
</tbody>
</table>

- In all of these cases reactants have a $G_f^0$ equal to zero, i.e., they are the reference forms of the elements
- so the $\Delta G^0$ is simply equal to the $G_f^0$ of the product compound

S&M: Example 2.4
- (pg 46)
- Dissolution of CO$_2$
- $\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq})$

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

**Fig. 2.7 Pg. 48**
Chromium Example (1/6)

Historically, chromium (Cr) has been used in numerous industrial processes, including leather tanning and metal plating operations. In these applications, if the water is mildly acidic, the Cr is typically present as bichromate (HCrO$_4^-$) and/or dichromate (Cr$_2$O$_7^{2-}$) ions. These ions can be interconverted by the reaction

$$2\text{HCrO}_4^- \leftrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$$

The standard Gibbs energies of formation of HCrO$_4^-$, Cr$_2$O$_7^{2-}$, and H$_2$O are $-764.8$, $-1301$, and $-237.18 \text{ kJ/mol}$, respectively.

a. Compute the equilibrium constant for the conversion of HCrO$_4^-$ to Cr$_2$O$_7^{2-}$.

b. Compute $G^o_{\text{eq}}$ as a function of the relative amounts of HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ in a system containing $10^{-4} \text{ M}$ total dissolved chromium ($c_{\text{Cr(III)}}$). Compare the condition of minimum chemical potential energy with the equilibrium condition as specified by the equilibrium constant. Assume all activity coefficients are 1.0.

c. Compute $\Delta G_r$ as a function of the HCrO$_4^-$ concentration for the solution described in part (b).

Example 2.10 from (pg 111): Benjamin, 2002

Chromium Example (2/6)

**Solution**

a. The reaction of interest is $2\text{HCrO}_4^- \leftrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$, for which the standard Gibbs energy of reaction is

$$\Delta G^o_r = G^o_{\text{Cr}_2\text{O}_7^{2-}} + G^o_{\text{H}_2\text{O}} - 2G^o_{\text{HCrO}_4^-}$$

$$\Delta G_r = [-1301 + (-237.18) -2(-764.8)] \text{ kJ/mol} = -8.58 \text{ kJ/mol}$$

Applying Equation (2.87), we obtain

$$\log K_{\text{eq}} = -\frac{\Delta G^o_r}{2.303RT}$$

b. The total Gibbs energy of the solution is the sum of the Gibbs energy contributions of the various constituents:

$$G_{\text{tot}} = n_{\text{H}_2\text{O}}(G^o_{\text{H}_2\text{O}} + RT \ln a_{\text{H}_2\text{O}}) + n_{\text{HCrO}_4^-}(G^o_{\text{HCrO}_4^-} + RT \ln a_{\text{HCrO}_4^-}) + n_{\text{Cr}_2\text{O}_7^{2-}}(G^o_{\text{Cr}_2\text{O}_7^{2-}} + RT \ln a_{\text{Cr}_2\text{O}_7^{2-}})$$

$$= (2.90)$$

Example 2.10 from (pg 111): Benjamin, 2002
Chromium Example (3/6)

where \( n_i \) is the number of moles of \( i \) in the system. Assuming that the system volume \( (V) \) is independent of the distribution of \( \text{Cr} \), \( V \) can be substituted for \( n_i \) for each species. Substituting molar concentrations for the activities of the chromium species, and setting the activity of water equal to its mole fraction \( (a_{H_2O} = c_{H_2O}/\sum c_i) \), we obtain.\(^{13}\)

\[
G_{\text{int}} = V_{H_2O} \left( \tilde{G}_{H_2O}^{\text{int}} + \frac{RT \ln \sum c_i}{c_{H_2O}} \right) + V_{\text{CrO}_4^{2-}} \left( \tilde{G}_{\text{CrO}_4^{2-}} + \frac{RT \ln c_{\text{CrO}_4^{2-}}}{c_{\text{CrO}_4^{2-}}} \right) \\
+ V_{\text{Cr}_2\text{O}_7^{2-}} \left( \tilde{G}_{\text{Cr}_2\text{O}_7^{2-}} + \frac{RT \ln c_{\text{Cr}_2\text{O}_7^{2-}}}{c_{\text{Cr}_2\text{O}_7^{2-}}} \right) \tag{2.91}
\]

\[
\frac{G_{\text{int}}}{V} = c_{H_2O} \left( \tilde{G}_{H_2O}^{\text{int}} + \frac{RT \ln \sum c_i}{c_{H_2O}} \right) + c_{\text{CrO}_4^{2-}} \left( \tilde{G}_{\text{CrO}_4^{2-}} + \frac{RT \ln c_{\text{CrO}_4^{2-}}}{c_{\text{CrO}_4^{2-}}} \right) \\
+ c_{\text{Cr}_2\text{O}_7^{2-}} \left( \tilde{G}_{\text{Cr}_2\text{O}_7^{2-}} + \frac{RT \ln c_{\text{Cr}_2\text{O}_7^{2-}}}{c_{\text{Cr}_2\text{O}_7^{2-}}} \right) \tag{2.92}
\]

Chromium Example (4/6)

The concentrations of \( \text{HCrO}_4^- \) and \( \text{Cr}_2\text{O}_7^{2-} \) are related to each other by stoichiometry. Furthermore, since 1 L of solution contains 55.56 mol of water, the mole fraction of water can be computed as a function of the concentration of either of the other species:

\[
c_{\text{Cr}_2\text{O}_7^{2-}} = 0.5(c_{\text{Cr}_2\text{O}_7^{2-}} - c_{\text{HCrO}_4^-}) = 0.5(0.10 - c_{\text{HCrO}_4^-}) \tag{2.93}
\]

\[
a_{H_2O} = \frac{55.56}{55.56 + c_{\text{HCrO}_4^-} + c_{\text{Cr}_2\text{O}_7^{2-}}} = \frac{55.56}{55.56 + 0.10 - c_{\text{HCrO}_4^-}} \tag{2.94}
\]
Chromium Example (5/6)

Substitution of Equations (2.93) and (2.94) into (2.92) yields a long but not complex expression for $G_{ex}$ per unit volume of solution in terms of a single variable, $c_{HCOO^-}$. The exact value of $c_{HCOO^-}$ where $G_{ex}/V$ is minimized could be found by differentiation with respect to $c_{HCOO^-}$. A plot of $G_{ex}/V$ versus $c_{HCOO^-}$ (Figure 2.8) indicates that the point of minimum Gibbs energy in the system (and hence the equilibrium condition) is at $c_{HCOO^-} = 0.0320$ mol/L, corresponding to $c_{CrO_2^{2-}} = 0.034$ mol/L. The activity (mole fraction) of water under these conditions is close to 0.999, so the activity quotient for the reaction is

$$Q = \frac{[CrO_2^{2-}][H_2O]}{[HCrO_4^-]^3} = \frac{0.034(0.999)}{(0.032)^3} = 33.2 \text{ ln } Q = 3.50$$

The computed value of $Q$ is essentially identical to the value of $K_{eq}$ computed in part (a). That is, the activity ratio indicates that when the total chemical potential energy of the system is minimized, $Q = K$, i.e., the reaction is at equilibrium. (The small difference between the computed values of $Q$ and $K$ is due to round-off error.)

Example 2.10 from (pg 111): Benjamin, 2002

Chromium Example (6/6)

- Minimum Gibbs free energy is where $\Delta G_r = 0$

Example 2.10 from (pg 111): Benjamin, 2002

---

**Figure 2.8** Total Gibbs energy per liter of a solution containing $HCIO_4^-$ and $CrO_2^{2-}$ as a function of the $HCOO^-$ concentration.

**Figure 2.9** The molar Gibbs energy of reaction for conversion of $HCIO_4^-$ to $CrO_2^{2-}$ in a system containing 0.1 M total Cr.
Alternative Direct Calculation

- Assume standard activity for water

\[ K = \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2} \]

- Combine equilibrium and mass balance equations

\[ Cr_{total} = 0.1 = [HCrO_4^-] + 2[Cr_2O_7^{2-}] \]

- Set bichromate = x

\[ 2[Cr_2O_7^{2-}] = 0.1 - x \]

\[ K = 32.5 = \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2} = \frac{0.05 - 0.5x}{x} \]

\[ 32.5x^2 + 0.5x - 0.05 = 0 \]

- And using the quadratic formula

\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.5 \pm \sqrt{0.25 - 6.5}}{65} = 0.032278 \]

Ionic Species & Redox

- Conventions

\[ G_f^o = 0, \text{ for } H_2 \]

\[ G_f^o = 0, \text{ for } H^+ \]

- this makes the hydrogen oxidation half reaction a reference point for Redox

\[ \text{for: } \frac{1}{2}H_2(g) = H^+ + e^-, \Delta G = 0 \]

- oxidations and reductions

\[ \text{must be coupled} \]

\[ \text{we only concern ourselves with the differences in } \Delta G \text{ for the two half reactions} \]
Temperature Effects on $K$

- Need $\Delta H$ (enthalpy change)
  - $\Delta H < 0$, exothermic (heat evolved)
  - $\Delta H > 0$, endothermic (heat absorbed)
- The Van’t Hoff Equation:

$$\log \frac{K_2}{K_1} = \frac{\Delta H^o (T_2 - T_1)}{2.303 RT_2 T_1}$$

- recall that:

$$\Delta H^o = \sum v_i \Delta H^o_i$$

Van’t Hoff Equation

- Where does it come from?

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

$$-RT \ln K = \frac{\Delta H^o}{R} - T \frac{\Delta S^o}{R}$$

$$\ln K = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

$$\frac{d \ln K}{dT} = \frac{\Delta H^o}{RT^2}$$

$$\int_{T_1}^{T_2} d \ln K = \int_{T_1}^{T_2} \frac{dT}{T^2}$$

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

- Gas fired

From: Quick Guide Plumbing, Creative Homeowner Press

A cross section of 1 & 1/2" copper pipe with a scale build-up of over 1/2" in thickness

Calcium scale formation on the inside of pipes and water heaters, on sinks, tubs, shower doors and other water contact surfaces is a multi-million dollar problem for individuals and businesses. A thin, one eighth inch layer of scale is such an effective insulator that it reduces the efficiency of your water heater by 20%. This translates directly to increased energy cost to attain the desired water temperature. Scale also increases the cost of equipment maintenance and shortens equipment life. When these costs are added together, the price of calcium scale is staggering.

<table>
<thead>
<tr>
<th>Thickness of Scale in Inches</th>
<th>Loss of Heat Transfer Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/16</td>
<td>15%</td>
</tr>
<tr>
<td>1/8</td>
<td>20%</td>
</tr>
<tr>
<td>1/4</td>
<td>39%</td>
</tr>
<tr>
<td>1/2</td>
<td>70%</td>
</tr>
<tr>
<td>3/4</td>
<td>90%</td>
</tr>
</tbody>
</table>

Data: US National Bureau of Standards
Example Problem

- Water is at equilibrium with calcium carbonate at 25°C. It enters a house at 15°C, then is heated to 60°C in a water heater.
  - Is the water supersaturated as it
    - A. enters the house?
    - B. leaves the water heater?

Solution to A.
- 1. Calculate $\Delta G^0$
- 2. Determine $K_1$ at 25°C
- 3. Determine $\Delta H^0$
- 4. Determine $K_2$ at 15°C

Solution

- At neutral pH: $\text{CaCO}_3\ (s) + \text{H}^+ = \text{HCO}_3^- + \text{Ca}^{+2}$
- 1. Calculate $\Delta G^0$
  - $=-140.31-132.18-(269.78) = -2.71$ kcal
- 2. Determine $K_1$ at 25°C
  - $\Delta G^0=-RT\ln K = -2.303RT\log K$
  - $-2.71=-2.303(0.001987)298\log K = 1.364\log K$
  - $\log K =1.99;\ K=10^{1.99}$
- 3. Determine $\Delta H^0$
  - $=-165.18-129.77-(288.345) = -6.5$ kcal
- 4. Determine $K_2$ at 15°C
  - $\log (K_2/10^{1.99}) = -6.5(288-298)/2.303(0.001987)288(298)=0.1655$
  - $\log K_2 = 2.156$
  - $K_2 = 10^{2.16}$
### Thermodynamic Constants for Species of Importance in Water Chemistry (Table 3-1 from Snoeyink & Jenkins) Part I

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H_f$ kcal/mole</th>
<th>$\Delta G_f$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{+2}$(aq)</td>
<td>-129.77</td>
<td>-132.18</td>
</tr>
<tr>
<td>CaCO$_3$(s), calcite</td>
<td>-288.45</td>
<td>-269.78</td>
</tr>
<tr>
<td>CaO (s)</td>
<td>-151.9</td>
<td>-144.4</td>
</tr>
<tr>
<td>C(s), graphite</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>-94.05</td>
<td>-94.26</td>
</tr>
<tr>
<td>CO$_2$(aq)</td>
<td>-98.69</td>
<td>-92.31</td>
</tr>
<tr>
<td>CH$_4$(g)</td>
<td>-17.889</td>
<td>-12.140</td>
</tr>
<tr>
<td>CH$_4$(aq)</td>
<td>-167.0</td>
<td>-149.00</td>
</tr>
<tr>
<td>HCO$_3^-$ (aq)</td>
<td>-165.18</td>
<td>-140.31</td>
</tr>
<tr>
<td>H$_2$CO$_3$(aq)</td>
<td>-167.0</td>
<td>-149.00</td>
</tr>
<tr>
<td>H$_2$O (g)</td>
<td>-57.7979</td>
<td>-54.6357</td>
</tr>
<tr>
<td>H$_2$O (l)</td>
<td>-68.3174</td>
<td>-56.690</td>
</tr>
<tr>
<td>HNO$_3$(aq)</td>
<td>-49.372</td>
<td>-26.43</td>
</tr>
<tr>
<td>HNO$_3$(aq)</td>
<td>-49.372</td>
<td>-26.43</td>
</tr>
<tr>
<td>Mn$^{+2}$(aq)</td>
<td>-53.3</td>
<td>-54.4</td>
</tr>
<tr>
<td>MnO$_2$(s)</td>
<td>-124.2</td>
<td>-111.1</td>
</tr>
</tbody>
</table>

### Thermodynamic Constants for Species of Importance in Water Chemistry (Table 3-1 from Snoeyink & Jenkins) Part II

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta H_f$ kcal/mole</th>
<th>$\Delta G_f$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{+2}$(aq)</td>
<td>-110.41</td>
<td>-108.99</td>
</tr>
<tr>
<td>Mg(OH)$_2$(s)</td>
<td>-221.00</td>
<td>-199.27</td>
</tr>
<tr>
<td>NO$_3^-$ (aq)</td>
<td>-49.372</td>
<td>-26.43</td>
</tr>
<tr>
<td>NH$_3$(g)</td>
<td>-11.04</td>
<td>-3.976</td>
</tr>
<tr>
<td>NH$_4^+$(aq)</td>
<td>-19.32</td>
<td>-6.37</td>
</tr>
<tr>
<td>NH$_4^+$(aq)</td>
<td>-31.74</td>
<td>-19.00</td>
</tr>
<tr>
<td>HNO$_3$(aq)</td>
<td>-49.372</td>
<td>-26.43</td>
</tr>
<tr>
<td>O$_2$(g)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O$_2$(g)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OH$^-$ (aq)</td>
<td>-54.957</td>
<td>-37.595</td>
</tr>
<tr>
<td>OH$^-$ (aq)</td>
<td>-54.957</td>
<td>-37.595</td>
</tr>
<tr>
<td>H$_2$O (g)</td>
<td>-57.7979</td>
<td>-54.6357</td>
</tr>
<tr>
<td>H$_2$O (l)</td>
<td>-68.3174</td>
<td>-56.690</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>-216.90</td>
<td>-177.34</td>
</tr>
<tr>
<td>HS (aq)</td>
<td>-4.22</td>
<td>3.01</td>
</tr>
<tr>
<td>HS(g)</td>
<td>-4.815</td>
<td>-7.892</td>
</tr>
<tr>
<td>H$_2$O(aq)</td>
<td>-9.4</td>
<td>-6.54</td>
</tr>
</tbody>
</table>
Solution (cont.)

- Repeat step #4 for 60°C.
- 4. Determine $K_2$ at 60°C
  - $\log \left( \frac{K_2}{10^{1.99}} \right) = \frac{-6.5(333-298)}{2.303(0.001987)333(298)} = -0.5$
  - $\log K_2 = 1.49$
  - $K_2 = 10^{1.49}$
- Compare $K_1$ and $K_2$ and $K_3$
  - what does this tell you about possible precipitation?
  - As temp increases, solubility decreases
  - This is an exothermic reaction, so rising temp drives reaction to the left

Le Chatelier’s Principle

- A system at equilibrium, when subject to a perturbation, responds in a way that tends to minimize its effect
  - If $\Delta H > 0$ (endothermic), $\frac{d\ln K}{dT} > 0$, and $K$↑ as T↑
    - if you heat endothermic reaction they will go further to the right
  - If $\Delta H < 0$ (exothermic), $\frac{d\ln K}{dT} < 0$, and $K$↓ as T↓
    - if you heat exothermic reaction they will go back to the left

$$\frac{d\ln K}{dT} = \frac{\Delta H^o}{RT^2}$$
Pressure & Temp. effects

- Temp
  \[ \left( \frac{\partial \Delta G^o}{\partial T} \right)_P = -\Delta S^o \]
- Pressure
  \[ \left( \frac{\partial \Delta G^o}{\partial P} \right)_T = \Delta V^o \]

Fig. 2.8
Pg. 56

To next lecture