For the reaction at 298 K,
\[ \text{P}_4\text{O}_{10} (s) + 6\text{H}_2\text{O} (l) \rightarrow 4\text{H}_3\text{PO}_4 (s) \]
the values of \( \Delta H^\circ \) and \( \Delta S^\circ \) are \(-416 \text{ kJ}\) and \(-209 \text{ J/K}\), respectively. What is the value of \( \Delta G^\circ \) at 298K?

We can calculate this using the Gibb’s relation:

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ
\]

\[
= -416 \text{ kJ} - (298 \text{ K})(-0.209 \frac{\text{kJ}}{\text{K}})
\]

\[
\Delta G^\circ = -354 \text{ kJ}
\]
Problem 2

Propane, a component in natural gas, can be used as a fuel in combustion reactions. What is the value for $\Delta G_{\text{non}}$ (in kJ) for the following reaction under the given conditions at 351 K?

$$C_3H_8 (g) + 5O_2 (g) \rightarrow 3CO_2 (g) + 4H_2O (g)$$

where $\Delta H^\circ_{\text{rxn}} = -2045$ kJ, $\Delta S^\circ_{\text{rxn}} = 103$ J/K, and $[C_3H_8] = 1.41$ M, $[O_2] = 1.99$ M, $[CO_2] = 7.27$ M, and $[H_2O] = 9.77$ M.

We can use the following expression to calculate nonstandard $\Delta G$:

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

However, we still have to figure out (standard) $\Delta G^\circ_{\text{rxn}}$ using the Gibb’s relation:

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

$$= -2045 \text{ kJ} - (351 \text{ K})(0.103 \frac{\text{ kJ}}{\text{ K}})$$

$$\Delta G^\circ = -2081 \text{ kJ}$$

Now, we can use the former equation:

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{[CO_2]^3[H_2O]^4}{[C_3H_8][O_2]^5}\right)$$

$$= -2081 \text{ kJ} + \left(0.008314 \frac{\text{ kJ}}{\text{ mol} \cdot \text{ K}}\right)(351 \text{ K})\ln\left(\frac{7.27^3 \cdot 9.77^4}{1.41^1 \cdot 1.99^5}\right)$$

$$= -2081 \text{ kJ} + 31 \text{ kJ}$$

$$\Delta G = -2050 \text{ kJ}$$
Problem 3

Balance the following *unbalanced* redox reaction (assume acidic solution if necessary):

\[ \text{Cl}_2 + \text{Cr}^{3+} \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{Cl}^- \]

You should follow the 7 steps for balancing redox equations.

1. **Split into half reactions:**
   - \( \text{Cl}_2 \rightarrow \text{Cl}^- \)
   - \( \text{Cr}^{3+} \rightarrow \text{Cr}_2\text{O}_7^{2-} \)

2. **Balance elements (not O or H):**
   - \( \text{Cl}_2 \rightarrow 2\text{Cl}^- \)
   - \( 2\text{Cr}^{3+} \rightarrow \text{Cr}_2\text{O}_7^{2-} \)

3. **Balance O with H\textsubscript{2}O:**
   - \( \text{Cl}_2 \rightarrow 2\text{Cl}^- \)
   - \( 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} \)

4. **Balance H with H\textsuperscript{+}:**
   - \( \text{Cl}_2 \rightarrow 2\text{Cl}^- \)
   - \( 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \)

5. **Balance charge with e\textsuperscript{−}’s:**
   - \( \text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^- \)
   - \( 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \)

6. **Make e\textsuperscript{−}’s equal:**
   - \( 3[\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-] \)
   - \( 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \)

7. **Add equations:**
   - \( 3\text{Cl}_2 + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Cl}^- \)
Problem 4

Calculate the standard potential ($E^\circ$) for the following non-balanced cell:

$$\text{MnO}_4^- (aq) + \text{Br}^- (aq) \leftrightarrow \text{Br}_2 (aq) + \text{Mn}^{2+} (aq)$$

Given:

$$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad E^\circ = 1.51 \text{ V}$$
$$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^- \quad E^\circ = 1.09 \text{ V}$$

Since they give you the non-balanced net reaction, we know that we should flip the second reaction (turning it from a reduction to an oxidation).

$$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad E^\circ = 1.51 \text{ V}$$
$$2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^- \quad E^\circ = -1.09 \text{ V}$$

You can then add these reactions to get the standard potential ($E^\circ$).*

$$E^\circ = 1.51 \text{ V} + (-1.09 \text{ V}) = 0.420 \text{ V}$$

*Notice that I didn’t balance this reaction. You could if you wanted to, but it isn’t necessary because we know that standard potential ($E^\circ$) is independent of stoichiometry. However, had they asked for something like free energy ($G$) then we would balance it since that quantity is dependent on the stoichiometry.
Problem 5

A galvanic cell is based on the following half-reactions at 297 K:

- \( \text{Na}^+ + e^- \rightarrow \text{Na} \)  \( E^\circ = -2.71 \text{ V} \)
- \( \text{H}_2\text{O}_2 (aq) + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \)  \( E^\circ = 1.78 \text{ V} \)

What will the potential of this cell be when \([\text{Na}^+] = 0.567 \text{ M}, [\text{H}^+] = 0.00307 \text{ M}\) and \([\text{H}_2\text{O}_2] = 0.801 \text{ M}\)?

We need to flip the first reaction to form a galvanic cell:

- \( \text{Na} (s) \rightarrow \text{Na}^+ (aq) + e^- \)  \( E^\circ = 2.71 \text{ V} \)
- \( \text{H}_2\text{O}_2 (aq) + 2\text{H}^+ (aq) + 2e^- \rightarrow 2\text{H}_2\text{O} (l) \)  \( E^\circ = 1.78 \text{ V} \)

Now form the net reaction and find \( E^\circ_{\text{cell}} \):

\[
2\text{Na} (s) + \text{H}_2\text{O}_2 (aq) + 2\text{H}^+ (aq) \rightarrow 2\text{Na}^+ (aq) + 2\text{H}_2\text{O} (l) \quad E^\circ_{\text{cell}} = 4.49 \text{ V}
\]

Now we can use the Nernst equation to calculate the nonstandard conditions (notice that \( n = 2 \text{ e}^- \)):

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln \left( \frac{[\text{Na}^+]^2}{[\text{H}^+]^2[\text{H}_2\text{O}_2]} \right)
\]

\[
= 4.49 \text{ V} - \frac{(8.314 \text{ J/mol K})(297 \text{ K})}{(2 \text{ mol e}^-)(96500 \text{ c mol e}^-)} \ln \left( \frac{(0.567)^2}{(0.00307)^2(0.801)} \right)
\]

\[
E_{\text{cell}} = 4.35 \text{ V}
\]
Problem 6

Which of the following species has the highest entropy?

Fe (s) — Incorrect because solids have less entropy than liquids and gases.

Ne (g) — Incorrect because this is monatomic gas. Gases generally have high entropy (more than liquids and solids); however Ne gas has less entropy than N₂O₂ gas because it is composed of single atoms.

H₂O (l) — Incorrect because liquids have less entropy than gases.

CH₃COOH (aq) — Incorrect because liquids have less entropy than gases, although aqueous solutions have more entropy than regular liquids.

N₂O₂ (g) — Correct: It is a gas, so it has higher entropy than the other solids and liquids (and aqueous solution). It also has higher entropy than Ne gas since Ne gas is monatomic while N₂O₂ gas is polyatomic, which has greater disorder (i.e. higher entropy).
Consider the reaction:

\[ A \text{ (aq)} + B \text{ (aq)} \leftrightarrow C \text{ (aq)} + D \text{ (aq)} \]

where \( \Delta H_{\text{rxn}} \) is negative and \( \Delta S_{\text{rxn}} \) is positive. What temperature will favor a spontaneous reaction when at standard conditions?

Remember that a spontaneous reaction is one in which \( \Delta G_{\text{rxn}} < 0 \) (i.e. negative).

And we know that we can determine that from the Gibb’s relation:

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

Since \( \Delta H_{\text{rxn}} \) is negative and \( \Delta S_{\text{rxn}} \) is positive:

\[ \Delta G_{\text{rxn}} = (\text{negative #}) - T(\text{positive #}) \]

This means that we are always subtracting a positive number (\( T\Delta S_{\text{rxn}} \)) from a negative number (\( \Delta H_{\text{rxn}} \)), meaning \( \Delta G_{\text{rxn}} \) will always be negative at all temperatures.
Problem 8

For the following two problems use the given half reactions to “construct” a galvanic cell.

\[
\begin{align*}
\text{Zn}^{2+} + 2e^- & \rightarrow \text{Zn} \quad E^\circ = -0.76 \text{ V} \\
\text{Cu}^{2+} + 2e^- & \rightarrow \text{Cu} \quad E^\circ = +0.34 \text{ V}
\end{align*}
\]

Which of the following statements about this galvanic cell is FALSE?

First form the net reaction by adding the equations:

\[
\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Cu} \quad E^\circ = +1.10 \text{ V}
\]

1. Negatively charged ions will flow from the salt bridge toward the anode.  
   True, anions flow to the anode and cations to the cathode.

2. Cu will be the electrode at the cathode.  True, because \( \text{Cu}^{2+} \) is being reduced to form \( \text{Cu} \) (s) and reduction takes place at the cathode.

3. Electrons will flow from the Zn electrode toward the Cu electrode.  True, because electrons will flow from the anode electrode (Zn) to the cathode electrode (Cu) through a wire.

4. The potential of this cell (at standard conditions) will be 1.10V.  True.

5. The mass of the Zn electrode will increase during the course of the reaction.  False, Zn will be oxidized to form \( \text{Zn}^{2+} \) so the mass of the Zn electrode will decrease.  We can also see that it’s a reactant from the net reaction above.
What is the pH of a 1.39 M solution of hypochlorous acid (HClO, $K_a = 2.9 \times 10^{-8}$)?

Write out acid dissociation reaction:

$$\text{HClO} \leftrightarrow \text{ClO}^- + \text{H}^+$$

Make an ICE chart since this is a weak acid equilibrium:

<table>
<thead>
<tr>
<th></th>
<th>HClO</th>
<th>$\leftrightarrow$</th>
<th>ClO$^-$</th>
<th>$+$</th>
<th>H$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.39</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>- x</td>
<td>+ x</td>
<td>+ x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1.39 - x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Write out $K_a$ and solve:

$$K_a = \frac{[\text{ClO}^-][\text{H}^+]}{[\text{HClO}]}$$

$$2.9 \times 10^{-8} \approx \frac{x^2}{1.39}$$

$$x = 0.0002 \text{ M} = [\text{H}^+]$$

$$\text{pH} = \log(0.0002)$$

$$\text{pH} = 3.70$$
Problem 10

A 1.0 L solution of CaF₂ was electrolyzed for 15.4 h to give 111.8 g of calcium. Assuming the minimum voltage needed was available, what ampage would be needed to complete the electrolysis in the given time?

First, break apart your salt to give the half reactions:

Reduction: \( \text{Ca}^{2+} + 2e^- \rightarrow \text{Ca} (s) \)

Oxidation: \( 2\text{F}^- \rightarrow \text{F}_2 + 2e^- \)

So, now we can use dimensional analysis:

\[
111.8 \text{ g Ca} \times \frac{1 \text{ mol Mg}}{40.1 \text{ g Mg}} \times \frac{2 \text{ mol } e^-}{1 \text{ mol Ca}} \times \frac{96,500 \text{ C}}{1 \text{ mol } e^-} = 538089.8 \text{ C}
\]

\[
538089.8 \text{ C} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ s}} = 9.71 \frac{\text{C}}{s}
\]

\( \rightarrow \) Remember that ampage is Coloumbs per second (i.e. C/s = A).
Consider the reaction:

\[ A \, (aq) \leftrightarrow B \, (aq) \]

at 299 K under standard conditions. If \( \Delta G^\circ \) is \(-5.07 \, \text{kJ}\) at this temperature, how much must the concentration of “reactant A” change for the non-standard Gibb’s Free energy to be \(-1.71 \, \text{kJ}\)?

We can use the following expression to relate the nonstandard and standard \( \Delta G \):

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

And we know that the reaction proceeds in such a fashion that:

\[
\begin{array}{l|cc}
\hline
   & A & \leftrightarrow & B \\
\hline
 I & 1.0 & 1.00 \\
 C & -x & +x \\
 E & 1.0 - x & 1.00 +x \\
\hline
\end{array}
\]

Standard conditions mean that \([A] = [B] = 1.0 \, \text{M}\)

\[
\Delta G = \Delta G^\circ + RT \ln \left( \frac{[B]}{[A]} \right)
\]

\[
-1.71 \, \text{kJ} = -5.07 \, \text{kJ} + \left( 0.008314 \, \frac{\text{kJ}}{\text{mol} \cdot \text{K}} \right) (299 \, \text{K}) \ln \left( \frac{1.0 + x}{1.0 - x} \right)
\]

\[
1.3516 = \ln \left( \frac{1.0 + x}{1.0 - x} \right)
\]

\[
3.864 = \frac{1.0 + x}{1.0 - x}
\]

\[
x = 0.589 \, \text{M}
\]
Problem 12

Consider the cell described below at 269 K:

\[ \text{Pb} | \text{Pb}^{2+} (1.33 \text{ M}) || \text{Fe}^{3+} (2.41 \text{ M}) | \text{Fe} \]

Given the standard reduction potentials found on the sheet attached to the exam, calculate the cell potential after the reaction has operated long enough for the [Fe\(^{3+}\)] to have changed by 1.468 M.

First, you need to recognize what is being reduced (cathode) and oxidized (anode):

<table>
<thead>
<tr>
<th>Cathode (Reduction)</th>
<th>Anode (Oxidation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}^{3+} + 3e^- \rightarrow \text{Fe} )</td>
<td>( \text{Pb} \rightarrow \text{Pb}^{2+} + 2e^- )</td>
</tr>
</tbody>
</table>

E\(^0\) = -0.036 V \hspace{1cm} E\(^0\) = +0.13 V

Now form the net reaction and find E\(^0\)\(_{\text{cell}}\):

\[ 2\text{Fe}^{3+} + 3\text{Pb} \rightarrow 3\text{Pb}^{2+} + 2\text{Fe} \]

E\(^0\)\(_{\text{cell}}\) = +0.094 V

Notice this is an galvanic cell (i.e. E\(^0\)\(_{\text{cell}}\) = positive)

Good, now set up your ICF chart:

<table>
<thead>
<tr>
<th></th>
<th>2Fe(^{3+})</th>
<th>+</th>
<th>3Pb</th>
<th>↔</th>
<th>3Pb(^{2+})</th>
<th>+</th>
<th>2Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2.41</td>
<td>--</td>
<td>1.33</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>- 2x</td>
<td>--</td>
<td>+ 3x</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>2.41 - 2x</td>
<td>--</td>
<td>1.33 + 3x</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

What’s x?

\[ 2x = 1.468 \]

\[ x = 0.734 \]

\[ \rightarrow \text{Now plug in } x \]

...continued on next slide...
Problem 12

Consider the cell described below at 269 K:

\[
\text{Pb} | \text{Pb}^{2+} (1.33 \text{ M}) \ || \ | \ | \text{Fe}^{3+} (2.41 \text{ M}) | \text{Fe}
\]

Given the standard reduction potentials found on the sheet attached to the exam, calculate the cell potential after the reaction has operated long enough for the \([\text{Fe}^{3+}]\) to have changed by 1.468 M.

So, we now have:

\[
\begin{array}{c|ccc}
 & 2\text{Fe}^{3+} & + & 3\text{Pb} & \leftrightarrow & 3\text{Pb}^{2+} & + & 2\text{Fe} \\
\hline
\text{I} & 2.41 & -- & 1.33 & -- \\
\text{C} & -1.468 & -- & +2.202 & -- \\
\text{F} & 0.942 & -- & 3.532 & -- \\
\end{array}
\]

\[
E^\circ_{\text{cell}} = +0.094 \text{ V}
\]

\[
n = 6 \text{ moles e}^-
\]

Now, just use Nernst Equation:

\[
E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln \left( \frac{[\text{Pb}^{2+}]^3}{[\text{Fe}^{3+}]^2} \right)
\]

\[
= 0.094 \text{ V} - \frac{(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}})(269 \text{ K})}{(6 \text{ mol e}^-)(96500 \frac{\text{C}}{\text{mol e}^-})} \ln \left( \frac{3.532^3}{0.942^2} \right)
\]

\[
E_{\text{cell}} = 0.0789 \text{ V}
\]

...continued from previous slide...
Problem 13

Consider the process of boiling Hg, which can be described as the phase change between the liquid and gaseous form. If the enthalpy of the reaction \( \Delta H^\circ_{\text{rxn}} \) = 58.5 kJ, and the boiling point of the reaction is 629.7 K, what is \( \Delta G^\circ_{\text{rxn}} \) at 289 K?

All phase changes occur at equilibrium, and we know that for a reaction at equilibrium: \( \Delta G^\circ_{\text{rxn}} = 0 \).

We know that we can calculate standard \( \Delta G^\circ_{\text{rxn}} \) for any temperature using the Gibb’s relation:

\[
G^\circ = H^\circ - T S^\circ
\]

We can rearrange this to solve for \( \Delta S^\circ_{\text{rxn}} \) since we are given \( \Delta H^\circ_{\text{rxn}} = 58.5 \) kJ, \( T = 629.7 \) K, and \( \Delta G^\circ_{\text{rxn}} = 0 \):

\[
S^\circ = \frac{H^\circ}{T} = \frac{58.5 \text{ kJ}}{629.7 \text{ K}} = 0.0929 \text{ kJ/K}
\]

Now, use the Gibb’s relation again but at \( T = 289 \) K:

\[
G^\circ = 58.5 \text{ kJ} \left( 289 \text{ K} \right) \left( 0.0929 \text{ kJ/K} \right) = 31.7 \text{ kJ}
\]
Problem 14

Consider a galvanic cell based on the following line notation at standard conditions and 298 K:

\[ \text{Sn} \mid \text{Sn}^{2+} \mid \text{Fe}^{3+} \mid \text{Fe} \]

Which of the following changes WILL NOT change the potential of the cell?

First form the net reaction:

\[ 2\text{Fe}^{3+} + 3\text{Sn} \rightarrow 2\text{Fe} + 3\text{Sn}^{2+} \]

1. Decrease the concentration of \( \text{Fe}^{3+} \). False, this will shift equilibrium to the left, so \( E^0 \) should decrease.
2. Add equal amounts of water to each half cell. False, this will decrease the concentrations of both \( \text{Fe}^{3+} \) and \( \text{Sn}^{2+} \), but \( \text{Sn}^{2+} \) more than \( \text{Fe}^{3+} \) (look at the stoichiometric coefficients). This will shift equilibrium to the right, so \( E^0 \) should increase.
3. Replace the Fe electrode with a Pt electrode. True, \( \text{Fe}^{3+} \) is being reduced to form Fe so replacing the Fe electrode with Pt will do nothing.
4. Replace the Sn electrode with a Pt electrode. False, Sn is being oxidized to form \( \text{Sn}^{3+} \) so replacing Sn with Pt will deplete the source of \( \text{Sn}^{3+} \).
5. Increase the concentration of \( \text{Sn}^{2+} \). False, this will shift equilibrium to the left, so \( E^0 \) should decrease.
Consider the following reaction at 347 K:

\[ \text{1A (aq) + 1B (aq) } \rightarrow \text{ 1C (aq) + 2D (aq)} \]

An experiment was performed with the following initial concentrations: \([A]_i = 1.35 \text{ M, } [B]_i = 2.13 \text{ M, } [C]_i = 0.57 \text{ M, } [D]_i = 0.29 \text{ M.} \] The reaction was allowed to proceed until equilibrium was reached at which time it was determined that \([A] = 0.67 \text{ M.} \] What is \(\Delta G_{\text{nonstandard}}\) at the initial conditions?

First, you should set up your ICE chart:

<table>
<thead>
<tr>
<th></th>
<th>1A</th>
<th>1B</th>
<th>1C</th>
<th>2D</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.35</td>
<td>2.13</td>
<td>0.57</td>
<td>0.29</td>
</tr>
<tr>
<td>C</td>
<td>-x</td>
<td>-x</td>
<td>+x</td>
<td>+2x</td>
</tr>
<tr>
<td>E</td>
<td>0.67</td>
<td>2.13-x</td>
<td>0.57+x</td>
<td>0.29+2x</td>
</tr>
</tbody>
</table>

At this point, you should figure out what ‘x’ is from the A column:

\[
1.35 \quad x = 0.67 \\
0.67 = 0.68
\]

And then we can plug this back into the ICE chart:

...continued on next slide...
Consider the following reaction at 347 K:

\[ \text{1A (aq) + 1B (aq) } \rightarrow \text{1C (aq) + 2D (aq)} \]

An experiment was performed with the following initial concentrations: \([A]_i = 1.35 \text{ M}, [B]_i = 2.13 \text{ M}, [C]_i = 0.57 \text{ M}, [D]_i = 0.29 \text{ M}. \] The reaction was allowed to proceed until equilibrium was reached at which time it was determined that \([A] = 0.67 \text{ M}.\] What is \(\Delta G_{\text{nonstandard}}\) at the initial conditions?

And then we can plug this back into the ICE chart:

<table>
<thead>
<tr>
<th></th>
<th>1A</th>
<th>+</th>
<th>1B</th>
<th>↔</th>
<th>1C</th>
<th>+</th>
<th>2D</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.35</td>
<td></td>
<td>2.13</td>
<td></td>
<td>0.57</td>
<td></td>
<td>0.29</td>
</tr>
<tr>
<td>C</td>
<td>-0.68</td>
<td>-0.68</td>
<td>+0.68</td>
<td>+2(0.68)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>0.67</td>
<td></td>
<td>1.45</td>
<td></td>
<td>1.25</td>
<td></td>
<td>1.65</td>
</tr>
</tbody>
</table>

Now we can solve for standard \(\Delta G^\circ\) from:

\[
\Delta G^\circ = G^\circ + RT \ln \left( \frac{[C][D]^2}{[A][B]} \right)
\]

\[
0 \text{ kJ} = \left( 3.62 \text{ kJ mol}^{-1} \text{ K}^{-1} \right) \left( \frac{347 \text{ K}}{1.25 \cdot 1.65^2} \right) \ln \frac{0.67 \cdot 1.45}{1.25 \cdot 1.65^2}
\]

\[\Delta G^\circ = 3.62 \text{ kJ}\]

...continued on next slide...
Problem 15

Consider the following reaction at 347 K:

\[ 1A \text{ (aq)} + 1B \text{ (aq)} \rightarrow 1C \text{ (aq)} + 2D \text{ (aq)} \]

An experiment was performed with the following initial concentrations: \([A]_i = 1.35 \text{ M}, [B]_i = 2.13 \text{ M}, [C]_i = 0.57 \text{ M}, [D]_i = 0.29 \text{ M}.\) The reaction was allowed to proceed until equilibrium was reached at which time it was determined that \([A] = 0.67 \text{ M}.\) What is \(\Delta G_{\text{nonstandard}}\) at the initial conditions?

But they want \(\Delta G_{\text{nonstandard}}\) at the initial conditions, so you have to plug in the initial concentrations given into the same equation:

\[
\Delta G = \Delta G^0 + RT \ln\left(\frac{[C][D]^2}{[A][B]}\right)
\]

\[
= 3.62 \text{ kJ} + 0.008314 \left(\frac{\text{kJ}}{\text{mol} \cdot \text{K}}\right) \left(347 \text{ K}\right) \ln\left(\frac{0.57 \cdot 0.29^2}{1.35 \cdot 2.13}\right)
\]

\[
\Delta G = 15.4 \text{ kJ}
\]

...continued from previous slides...
Which of the following statements about spontaneity are true?

1. A reaction with an increase in enthalpy and entropy will be spontaneous at all temperatures. False, this means that $\Delta H$ and $\Delta S$ are positive. Using the Gibb’s relation these reactions will only be spontaneous at high temperatures.

2. The enthalpy change in a reaction can be used to predict if a reaction will be spontaneous or not. False, only change in Gibb’s free energy ($\Delta G$) can be used to indicate spontaneity.

3. A reaction with a negative value for $\Delta G_{\text{nonstandard}}$ will result in only products being present at the end of the reaction. False, while a negative $\Delta G$ does tell us this will be spontaneous, it does not mean that the reaction will proceed to completion (i.e. only products).

4. A decrease in the entropy of the reaction ensures that only reactants will be formed during the course of a reaction. False.

5. A reaction with a positive value for $\Delta G_{\text{nonstandard}}$ will result in some amount of products being present at the end of the reaction. True, this is what statement 3 got wrong.
At 277 K a 2.29 M solution of formic acid is found to have a pH of 1.6924. What is the ΔG° for this reaction?

Since this is a weak acid, we can set up the following ICE chart:

<table>
<thead>
<tr>
<th></th>
<th>HCO₂H</th>
<th>↔</th>
<th>CO₂H⁻ + H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2.29</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>- x</td>
<td>+ x</td>
<td>+ x</td>
</tr>
<tr>
<td>E</td>
<td>2.29 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

From the given pH of 1.6924 we can determine the [H⁺] (‘x’ in the ICE chart):

\[
pH = \log[H^+] \\
1.6924 = \log[H^+] \\
[H^+] = 0.0203 \text{ M}
\]

We can now complete the ICE chart above:

<table>
<thead>
<tr>
<th></th>
<th>HCO₂H</th>
<th>↔</th>
<th>CO₂H⁻ + H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2.29</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>- 0.0203</td>
<td>+ 0.0203</td>
<td>+ 0.0203</td>
</tr>
<tr>
<td>E</td>
<td>2.2697</td>
<td>0.0203</td>
<td>0.0203</td>
</tr>
</tbody>
</table>

...continued on next slide...
At 277 K a 2.29 M solution of formic acid is found to have a pH of 1.6924. What is the $\Delta G^\circ$ for this reaction?

We can now complete the ICE chart above:

<table>
<thead>
<tr>
<th></th>
<th>$\text{HCO}_2\text{H}$</th>
<th>$\text{CO}_2\text{H}^-$</th>
<th>$\text{H}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2.29</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>-0.0203</td>
<td>+0.0203</td>
<td>+0.0203</td>
</tr>
<tr>
<td>E</td>
<td>2.2697</td>
<td>0.0203</td>
<td>0.0203</td>
</tr>
</tbody>
</table>

We know that we can always relate equilibrium concentrations ($K_{eq}$) to standard $\Delta G^\circ$ using the following relationship:

$$G^\circ = RT\ln\left(K_{eq}\right)$$

$$= RT\ln\left(\frac{[\text{CO}_2\text{H}^-][\text{H}^+]}{[\text{HCO}_2\text{H}]}\right)$$

$$= \left(0.008314 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}\right) \left(277 \text{ K}\right)\ln\left(\frac{0.0203 \cdot 0.0203}{2.2697}\right)$$

$$G^\circ = 19.9 \text{ kJ}$$

...continued from previous slide...
Problem 18

A concentration cell based on the following half reaction at 284 K

\[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \quad E^° = -0.76 \text{ V} \]

has initial concentrations of 1.29 M Zn\(^{2+}\), 0.317 M Zn\(^{2+}\), and a potential of 0.01717 V at these conditions. After 9.4 hours, the new potential of the cell is found to be 0.003480 V. What is the concentration of Zn\(^{2+}\) at the cathode at this new potential?

I like to think of concentration cells as “special galvanic cells” so we still have:

- \[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \quad ; \quad E^° = +0.76 \text{ V} \quad \leftarrow \text{C = Cathode: Reduction} \]

- \[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad ; \quad E^° = -0.76 \text{ V} \quad \leftarrow \text{A = Anode: Oxidation} \]

And we can form a “special” net reaction: I label where each come from w/ A or C

<table>
<thead>
<tr>
<th></th>
<th>Zn(^{2+}) [C] + Zn [A] ↔ Zn(^{2+}) [A] + Zn [C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.29 -- 0.317 --</td>
</tr>
<tr>
<td>C</td>
<td>- x -- + x --</td>
</tr>
<tr>
<td>F</td>
<td>1.29 - x 0.317 + x --</td>
</tr>
</tbody>
</table>

\[ E^°_{\text{cell}} = 0.0 \text{ V} \]

Now let’s use Nernst for \(T = 284 \text{ K}\) and \(E_{\text{cell}} = 0.003480 \text{ V}\):

...continued on next slide...
A concentration cell based on the following half reaction at 284 K

\[ \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \quad E^o = -0.76 \text{ V} \]

has initial concentrations of 1.29 M Zn\(^{2+}\), 0.317 M Zn\(^{2+}\), and a potential of 0.01717 V at these conditions. After 9.4 hours, the new potential of the cell is found to be 0.003480 V. What is the concentration of Zn\(^{2+}\) at the cathode at this new potential?

Now let’s use Nernst for \( T = 284 \text{ K} \) and \( E_{\text{cell}} = 0.003480 \text{ V} \):

\[
E_{\text{cell}} = E^o_{\text{cell}} + \frac{RT}{nF} \ln \left( \frac{[\text{Zn}^{2+}]_{\text{Anode}}}{[\text{Zn}^{2+}]_{\text{Cathode}}} \right)
\]

\[
0.003480 \text{ V} = 0.0 \text{ V} + \frac{(8.314 \text{ J mol}^{-1} \text{K}^{-1})(284 \text{ K})}{(2 \text{ mol e}^-)(96500 \text{ C mol}^{-1} \text{e}^-)} \ln \left( \frac{0.317 + x}{1.29 x} \right)
\]

\[
-0.2815 = \ln \left( \frac{0.317 + x}{1.29 x} \right) \Rightarrow x = 0.371
\]

Now we can determine the concentration of Zn\(^{2+}\) at the cathode:

\[
[Zn^{2+}]_{\text{Cathode}} = 1.29 x
\]

\[
= 0.917 \text{ M}
\]

...continued from previous slide...
Consider the reaction:

\[ A (aq) \leftrightarrow B (aq) \]

at 295 K where the initial concentration of A = 1.00 M and the initial concentration of B = 0.000 M. At equilibrium it is found that the concentration of B = 0.595 M. What is the maximum amount of work that can be done by this system when the concentration of A = 0.859 M?

We have the following ICE chart:

<table>
<thead>
<tr>
<th></th>
<th>A (aq)</th>
<th>B (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>E</td>
<td>1-x</td>
<td>x</td>
</tr>
</tbody>
</table>

At equilibrium, we know [B] = 0.595 M, so \(x = 0.595\)

We can use this \(x\) to plug back into the ICE chart!
Problem 19

Consider the reaction:

\[ \text{A (aq)} \rightleftharpoons \text{B (aq)} \]

at 295 K where the initial concentration of A = 1.00 M and the initial concentration of B = 0.000 M. At equilibrium it is found that the concentration of B = 0.595 M. What is the maximum amount of work that can be done by this system when the concentration of A = 0.859 M?

We can use this \( x = 0.595 \) to plug back into the ICE chart!

| \[ \text{A (aq)} \rightleftharpoons \text{B (aq)} \] |
|---|---|
| I | 1.00 | 0 |
| C | -0.595 | +0.595 |
| E | 0.405 | 0.595 |

Now we can evaluate \( \Delta G^\circ \) from Equilibrium conditions

\[
G = G^\circ + RT \ln(Q)
\]

\[
0 = G^\circ + RT \ln(K)
\]

\[
G^\circ = (8.314 \text{ J/mol} \cdot \text{K})(295 \text{ K}) \ln\left(\frac{0.595}{0.405}\right)
\]

\[
G^\circ = 943.46 \text{ J/mol}
\]

...continued from previous slide...
Problem 19

Consider the reaction:

\[ A \text{ (aq)} \leftrightarrow B \text{ (aq)} \]

at 295 K where the initial concentration of A = 1.00 M and the initial concentration of B = 0.000 M. At equilibrium it is found that the concentration of B = 0.595 M. What is the maximum amount of work that can be done by this system when the concentration of A = 0.859 M?

We can repeat this to find x = 0.141 to plug back into an ICE chart again:

<table>
<thead>
<tr>
<th></th>
<th>A (aq)</th>
<th>B (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>-0.141</td>
<td>+0.141</td>
</tr>
<tr>
<td>E</td>
<td>0.859</td>
<td>0.141</td>
</tr>
</tbody>
</table>

Now we can evaluate \( \Delta G \) from Equilibrium conditions

\[
G = G^o + RT\ln(Q)
\]

\[
= 943.46 \frac{\text{J}}{\text{mol}} + (8.314 \frac{\text{J}}{\text{molK}})(295 \text{ K})\ln\left(\frac{0.141}{0.859}\right)
\]

\[
G = 53800 \frac{\text{J}}{\text{mol}}
\]

...continued from previous slide...
Consider a cell based on the following line notation at 289 K:

\[ \text{Sn | Sn}^{2+} (1.33 \text{ M}) \mid \mid \text{Pb}^{2+} (2.27 \text{ M}) \mid \text{Pb} \]

**Given:**

\[
\begin{align*}
Pb^{2+} + 2e^- & \rightarrow Pb ; \quad E^0 = -0.131 \text{ V} \quad \text{Cathode: Reduction} \\
Sn^{2+} + 2e^- & \rightarrow Sn ; \quad E^0 = -0.143 \text{ V} \quad \text{Anode: Oxidation (flip)}
\end{align*}
\]

**What will the concentration of the Pb\(^{2+}\) solution be when the cell is dead?**

Now form the net reaction and find \(E_{\text{cell}}^0\):

\[
Pb^{2+} + Sn \rightarrow Sn^{2+} + Pb ; \quad E^0_{\text{cell}} = 0.012 \text{ V}
\]

Notice this is a galvanic cell (i.e. \(E_{\text{cell}}^0 = \text{positive}\))

Good, now set up your ICF chart:

<table>
<thead>
<tr>
<th></th>
<th>Pb(^{2+})</th>
<th>Sn</th>
<th>(\leftrightarrow)</th>
<th>Sn(^{2+})</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2.27</td>
<td>--</td>
<td>1.33</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>- x</td>
<td>--</td>
<td>+ x</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>2.27 (- x)</td>
<td>--</td>
<td>1.33 + x</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

Now for a dead battery \(E_{\text{cell}} = 0 \text{ V}\), so let’s use the Nernst equation:

\[
E_{\text{cell}} = E_{\text{cell}}^0 + \frac{RT}{nF} \ln \left( \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} \right)
\]

...continued on next slide...
Problem 20

Consider a cell based on the following line notation at 289 K:

\[ \text{Sn} \mid \text{Sn}^{2+} (1.33 \text{ M}) \mid \mid \text{Pb}^{2+} (2.27 \text{ M}) \mid \text{Pb} \]

Given:

\[ \text{Pb}^{2+} + 2e^- \rightarrow \text{Pb} ; \quad E^0 = -0.131 \text{ V} \quad \leftarrow \text{Cathode: Reduction} \]

\[ \text{Sn}^{2+} + 2e^- \rightarrow \text{Sn} ; \quad E^0 = -0.143 \text{ V} \quad \leftarrow \text{Anode: Oxidation (flip)} \]

What will the concentration of the \( \text{Pb}^{2+} \) solution be when the cell is dead?

\[
\begin{array}{c|ccc}
 & \text{Pb}^{2+} & + & \text{Sn} & \Leftrightarrow & \text{Sn}^{2+} & + & \text{Pb} \\
\hline
I & 2.27 & -- & 1.33 & -- \\
C & -x & -- & +x & -- \\
F & 2.27 - x & -- & 1.33 + x & -- \\
\end{array}
\]

Using Nernst for a dead battery:

\[
0 = 0.012 \text{ V} \left( \frac{8.314 \text{ J}}{\text{mol} \cdot \text{K}} \right) \left( 289 \text{ K} \right) \ln \left( \frac{1.33 + x}{2.27 - x} \right)
\]

\[
0.964 = \ln \left( \frac{1.33 + x}{2.27 - x} \right) \Rightarrow 2.622 = \frac{1.33 + x}{2.27 - x}
\]

\[
x = 1.271 \text{ M}
\]

So,

\[
[\text{Pb}^{2+}] = 2.27 \quad 1.271 = 0.999 \text{ M}
\]

...continued from previous slide...
Problem 21

Which of the following statements about Gibb’s Free Energy is true?

1. The value of $\Delta G_{\text{nonstandard}}$ for a reaction will always be negative when products are observed being formed in the reaction. **False**, products can also be formed at positive $\Delta G_{\text{nonstandard}}$ (though probably very little), or $\Delta G_{\text{nonstandard}} = 0$ (equilibrium, meaning equal reactant and product formation).

2. If the value of $\Delta G_{\text{nonstandard}}$ is negative at the beginning of the reaction, the sign of $\Delta G^\circ$ will also be negative. **False**, $\Delta G = \Delta G^\circ + RT\ln(Q)$. From that equation we can see that this does not need to be true.

3. If $\Delta G^\circ$ for a reaction is negative, the equilibrium position will lie on the side of the products. **True**, a negative $\Delta G^\circ$ tells us that products will be formed spontaneously and favorably.

4. The sign of $\Delta G^\circ$ is always the same as $\Delta S_{\text{universe}}$. **False**.

5. The more negative the value for $\Delta G_{\text{nonstandard}}$, the smaller the driving force for the formation of the products. **False**, the more negative $\Delta G_{\text{nonstandard}}$ is, the larger the driving force is for product formation.
Problem 22

A concentration cell is built based on the reaction:

\[ 2H^+ + 2e^- \rightarrow H_2 \]

The pH in one of the half cells is –0.2529, while the pH in the other is 2.742. If the temperature of the overall cell is 298 K, what is the potential?

I like to think of concentration cells as "special galvanic cells" so we have:

- **C = Cathode: Reduction → Higher concentration**
- **A = Anode: Oxidation → Lower concentration**

And we can form a "special" net reaction: I label where each come from w/ A or C

\[
\begin{array}{ccc}
2H^+ [C] + H_2 [A] & \leftrightarrow & 2H^+ [A] + H_2 [C] \\
\hline
?? & -- & ??? & -- \\
\end{array}
\]

E° \text{cell} = 0.0 V

Use the pH's to determine the concentration of H^+ in each cell.

\[ \text{pH} = \log[H^+] \quad \text{pH} = \log[H^+] \]

\[ 0.2529 = \log[H^+] \quad 2.742 = \log[H^+] \]

\[ [H^+] = 1.7902 \text{ M} \quad [H^+] = 0.0018 \text{ M} \]

Remember that the higher concentration is the Cathode. So now we can plug these values into the Nernst equation:

...continued on next slide...
Problem 22

A concentration cell is built based on the reaction:

\[ 2H^+ + 2e^- \rightarrow H_2 \]

The pH in one of the half cells is \(-0.2529\), while the pH in the other is \(2.742\). If the temperature of the overall cell is \(298\, \text{K}\), what is the potential?

Remember that the higher concentration is the Cathode. So now we can plug these values into the Nernst equation:

| \[ 2H^+ \, [C] + H_2 \, [A] \leftrightarrow 2H^+ \, [A] + H_2 \, [C] \] |
|------------------|------------------|------------------|------------------|------------------|
| 1.7902 | -- | 0.0018 | -- |

\[ E^\circ_{\text{cell}} = 0.0 \, \text{V} \]

\[
E_{\text{cell}} = E^\circ_{\text{cell}} \frac{RT}{nF} \ln \left( \frac{[H^+]^2_{\text{Anode}}}{[H^+]^2_{\text{Cathode}}} \right)
\]

\[
= 0.0 \, \text{V} \frac{(8.314 \, \text{J/molK})(298 \, \text{K})}{(2 \, \text{mol e}^-)(96500 \, \text{C/mol e}^-)} \ln \left( \frac{0.0018^2}{1.7902^2} \right)
\]

\[ E_{\text{cell}} = 0.177 \, \text{V} \]