1. Draw the Eh-pH diagram for the Co-H₂O system assuming ionic activities are all $10^{-3}$. What is the Co²⁺ activity if $E=0.25$ V and $pH=6.0$. If cobalt metal is maintained at a potential of 0 Volts in a solution at $pH=7.5$, what will happen to the cobalt metal?

The free energy of formation data is given below:

<table>
<thead>
<tr>
<th>Species</th>
<th>$\Delta G_{formation}^{o}, (\text{cal / mole})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO</td>
<td>-52,310</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>-167,835</td>
</tr>
<tr>
<td>Co₂O₃</td>
<td>-115,130</td>
</tr>
<tr>
<td>CoO₂</td>
<td>-54,840</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>-12,800</td>
</tr>
<tr>
<td>HCoO₂⁻</td>
<td>-82,970</td>
</tr>
<tr>
<td>Co³⁺</td>
<td>28,900</td>
</tr>
</tbody>
</table>

The Eh-pH diagram is shown in Figure 1. The equations for all the lines considered are given below.

\[
\text{Co}^{2+} + 2H_2O \leftrightarrow \text{HCoO}_2^- + 3H^+ \quad \log \frac{[\text{HCoO}_2^-]}{[\text{Co}^{2+}]} = -31.70 + 3pH
\]

\[
\text{Co}^{2+} \leftrightarrow \text{Co}^{3+} + e^- \quad E = 1.808 + 0.059 \log \frac{[\text{Co}^{3+}]}{[\text{Co}^{2+}]} 
\]

\[
\text{Co}^{3+} + 2H_2O + e^- \leftrightarrow \text{HCoO}_2^- + 3H^+ \quad E = -0.065 + 0.1773pH + 0.059 \log \frac{[\text{HCoO}_2^-]}{[\text{Co}^{3+}]} 
\]

\[
< \text{Co} > + H_2O \leftrightarrow \text{CoO} > + 2H^+ + 2e^- \quad E = 0.095 - 0.059pH
\]

\[
3 < \text{CoO} > + H_2O \leftrightarrow < \text{Co}_3O_4 > + 2H^+ + 2e^- \quad E = 0.993 - 0.059pH
\]

\[
2 < \text{Co}_3O_4 > + H_2O \leftrightarrow 3 < \text{Co}_2O_3 > + 2H^+ + 2e^- \quad E = 1.018 - 0.059pH
\]

\[
< \text{Co}_2O_3 > + H_2O \leftrightarrow 2 < \text{Co}_2O_2 > + 2H^+ + 2e^- \quad E = 1.477 - 0.059pH
\]

\[
\text{Co}^{2+} + H_2O \leftrightarrow < \text{CoO} > + 2H^+ \quad \log([\text{Co}^{2+}]) = 12.6 - 2pH
\]

\[
< \text{CoO} > + H_2O \leftrightarrow \text{HCoO}_2^- + H^+ \quad \log([\text{HCoO}_2^-]) = -19.10 + pH
\]


\[ 2\text{Co}^{3+} + 3H_2O \leftrightarrow \text{Co}_2O_3 + 6H^+ \quad \log(\text{Co}^{3+}) = -1.05 - 3pH \]

\[ < \text{Co} > \leftrightarrow \{ \text{Co}^{2+} \} + 2e^- \quad E = -0.277 + 0.0295\log(\text{Co}^{2+}) \]

\[ < \text{Co} > + 2H_2O \leftrightarrow \{ \text{HCoO}_2^- \} + 3H^+ + 2e^- \quad E = 0.659 - 0.089pH + 0.0295\log(\text{HCoO}_2^-) \]

\[ 3\text{Co}^{2+} + 4H_2O \leftrightarrow < \text{Co}_3O_4 > + 8H^+ + 2e^- \quad E = 2.11 - 0.236pH - 0.089\log(\text{Co}^{2+}) \]

\[ 2\{ \text{HCoO}_2^- \} + H^+ \leftrightarrow < \text{Co}_3O_4 > + 2H_2O + 2e^- \quad E = -0.70 + 0.0295pH - 0.089\log(\text{HCoO}_2^-) \]

\[ 2\{ \text{Co}^{2+} \} + 3H_2O \leftrightarrow < \text{Co}_2O_3 > + 6H^+ + 2e^- \quad E = 1.75 - 0.177pH - 0.059\log(\text{Co}^{2+}) \]

\[ 2\{ \text{HCoO}_2^- \} \leftrightarrow < \text{Co}_2O_3 > + H_2O + 2e^- \quad E = -0.128 - 0.059\log(\text{HCoO}_2^-) \]

\[ \{ \text{Co}^{2+} \} + 2H_2O \leftrightarrow < \text{Co}_2O_2 > + 4H^+ + 2e^- \quad E = 1.61 - 0.118pH - 0.0295\log(\text{Co}^{2+}) \]

\[ \{ \text{Co}^{3+} \} + 2H_2O \leftrightarrow < \text{Co}_2O_2 > + 4H^+ + e^- \quad E = 1.42 - 0.236pH - 0.059\log(\text{Co}^{3+}) \]

Figure 1. Eh-pH diagram for cobalt with ion activities of 0.001.
For the second part of the question, the above equations must be used. For \(E=0.25\), \(pH=6\), this is in the \(\text{Co}^{2+}\) stability region, the \(\text{Co}^{2+}\) ion activity must be 0.001. Maintaining cobalt metal at \(E=0\) and \(pH=7.5\) again gives the stable species as \(\text{Co}^{2+}\) ion. Therefore, the metal will be leached/corroded to \(\text{Co}^{2+}\) ions.

2. Aluminum metal was completely dissolved in an acidic solution and the total Al concentration was measured to be 0.01 M. Graph the equilibrium concentration of each Al species as a function of pH over the range \(1<pH<14\) from the data given below.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>({\text{Al}^{3+}} + {\text{H}_2\text{O}} \Leftrightarrow {\text{Al(OH)}^{2+}} + {\text{H}^+})</td>
<td>(K_1 = 2.04\times10^{-6})</td>
</tr>
<tr>
<td>({\text{Al}^{3+}} + 2{\text{H}_2\text{O}} \Leftrightarrow {\text{Al(OH)}_3^+} + 2{\text{H}^+})</td>
<td>(K_2 = 5.01\times10^{-10})</td>
</tr>
<tr>
<td>({\text{Al}^{3+}} + 3{\text{H}_2\text{O}} \Leftrightarrow {\text{Al(OH)}_3} + 3{\text{H}^+})</td>
<td>(K_3 = 1.00\times10^{-15})</td>
</tr>
<tr>
<td>({\text{Al}^{3+}} + 4{\text{H}_2\text{O}} \Leftrightarrow {\text{Al(OH)}_3} + 4{\text{H}^+})</td>
<td>(K_4 = 1.00\times10^{-23})</td>
</tr>
<tr>
<td>({\text{Al}^{3+}} + 3{\text{H}_2\text{O}} \Leftrightarrow &lt;\text{Al(OH)}_3&gt; + 3{\text{H}^+})</td>
<td>(K_5 = 3.16\times10^{-9})</td>
</tr>
</tbody>
</table>

The total Al is the total concentration in solution; therefore, \(K_5\) is not needed at this time. The equation relating \(\{\text{Al}^{3+}\}\), \(\{\text{H}^+\}\), Al_{tot} and the K-values is:

\[
\{\text{Al}^{3+}\} = \frac{\text{Al}_{\text{tot}}}{(1 + \frac{K_1}{\text{H}^+} + \frac{K_2}{(\text{H}^+)^2} + \frac{K_3}{(\text{H}^+)^3} + \frac{K_4}{(\text{H}^+)^4})} \]

with the \(\{\text{Al}^{3+}\}\) then the concentration of each species can be calculated. The diagram for all the aqueous species is shown in Figure 2. <\text{Al(OH)}_3> precipitates between about pH 3 and 12.

In addition, one could consider that the Al_{tot} includes the precipitated solid species, which is more likely to be the way experiments are run. In this case the \(\{\text{Al}^{3+}\}\) equation is:

\[
\{\text{Al}^{3+}\} = \frac{\text{Al}_{\text{tot}}}{(1 + \frac{K_1}{\text{H}^+} + \frac{K_2}{(\text{H}^+)^2} + \frac{K_3}{(\text{H}^+)^3} + \frac{K_4}{(\text{H}^+)^4} + \frac{K_5}{(\text{H}^+)^5})} \]

and Figure 3 shows the resulting distribution of species diagram. This diagram is equivalent to Eh-pH diagram for Al-H_2O.
Figure 2. Distribution of aluminum hydroxide species as a function of pH.

Figure 3. Distribution of aluminum hydroxide species as a function of pH with $<$Al(OH)$_3$> included.
3. Evaluate the activity coefficient of Ca\(^{2+}\) in the following solutions:

a. 0.004 M HCl, 0.02 M CaCl\(_2\), T=298 K using both the mean salt method and the Debye-Hückel equations.

b. 0.0004 M HCl, 0.002 M CaCl\(_2\), T=298 K and 318 K using the Debye-Hückel equation.

To use the mean salt method and the Debye-Hückel method, their equations need to be identified:

Mean salt: \[ \gamma_{Ca^{2+}} = \frac{\gamma_{CaCl_2}^3}{\gamma_{KCl}^2} \]

Debye-Hückel: \[ \log \gamma_{Ca^{2+}} = -\frac{Az^2\sqrt{I}}{1 + Ba\sqrt{I}} \]

Therefore, the mean activity coefficients of calcium chloride and potassium chloride must be found. These values need the molality of the species. It will be assumed that the temperature and pressure are such that the solvent density equals water density equals 1 g/ml, so that molality and molarity are equal. For the DH method, the constants A and B, the ionic strength and the ionic size must be found.

a. Mean salt – molality CaCl\(_2\) = 0.02 - \(\gamma_{0.01}\)=0.725 and \(\gamma_{0.05}\)=0.57 and by interpolation \([(0.725-0.57)/(0.01-0.05)] = -3.875 so that \(\gamma_{0.02}\) = 0.725-3.875*(0.02-0.01) = 0.686.

Molality of KCl= molality of Cl = 0.004 + 2*0.02=0.44. Again, the activity coefficient must be found by interpolation. \([(0.651-0.719)/(0.5-0.2)]=-0.2267. The 0.44 activity coefficient value is 0.651+(0.44-0.5)*-0.2267=0.6646. Thus

\[ \gamma_{Ca^{2+}} = \frac{\gamma_{CaCl_2}^3}{\gamma_{KCl}^2} = \frac{0.686^3}{0.6646^2} = 0.731 \text{ by the mean salt method.} \]

For the DH method A=0.5085 and B=0.3281x10\(^8\), and \(a=6x10^{-8}\). The ionic strength is \(I=(\Sigma z^2C)/2=(0.004+0.004+4*0.02+0.04)/2=0.064\)

\[ \log \gamma_{Ca^{2+}} = -\frac{Az^2\sqrt{I}}{1 + Ba\sqrt{I}} = -\frac{0.585 * 4 \sqrt{0.064}}{1 + 0.3281 * 6 \sqrt{0.064}} = -0.5920 \text{ and} \]
\[ \gamma_{Ca^{2+}} = 10^{-0.395} = 0.403 \text{ which isn’t all that close to the mean salt method value.} \]

b. For this part of the question, A and B at each temperature are needed as is the new ionic strength. At 318 K, A=0.5271 and B=0.3314x10\(^8\). \(I=(\Sigma z^2C)/2=(0.004+0.004+4*0.02+0.04)/2 = 0.0064. Thus, the DH equation at 298 K is
\[ \log \gamma_{\text{Ce}^{2+}} = -\frac{A_{\text{Ce}^{2+}} \sqrt{I}}{1 + B_{\text{Ce}^{2+}} \sqrt{I}} = -\frac{0.585 \times 4 \times \sqrt{0.0064}}{1 + 0.3281 \times 6 \times \sqrt{0.0064}} = -0.1872 \quad \frac{1.157}{1} = -0.162 \quad \text{and} \]

\[ \gamma_{\text{Ce}^{2+}} = 10^{-0.162} = 0.689. \quad \text{At } 318 \text{ } \text{K the equations become} \]

\[ \log \gamma_{\text{Ce}^{2+}} = -\frac{A_{\text{Ce}^{2+}} \sqrt{I}}{1 + B_{\text{Ce}^{2+}} \sqrt{I}} = -\frac{0.5271 \times 4 \times \sqrt{0.0064}}{1 + 0.3314 \times 6 \times \sqrt{0.0064}} = -0.1687 \quad \frac{1.159}{1} = -0.146 \quad \text{and} \]

\[ \gamma_{\text{Ce}^{2+}} = 10^{-0.146} = 0.714. \]
4. The initial reaction rates between halides organic X and Y with hydroxide ion are given below. Find the reaction order with respect to each of the reactants and the rate constant. What will happen if both X and Y are present with hydroxide ions in the same solution and initially at the same concentration.

**Reaction X:**

<table>
<thead>
<tr>
<th>[X]₀, M</th>
<th>0.1</th>
<th>0.2</th>
<th>0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>[OH]₀, M</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Initial rate, 1/(M·s)</td>
<td>2.1x10⁻³</td>
<td>4.2x10⁻³</td>
<td>8.1x10⁻³</td>
</tr>
</tbody>
</table>

**Reaction Y:**

<table>
<thead>
<tr>
<th>[Y]₀, M</th>
<th>0.002</th>
<th>0.004</th>
<th>0.002</th>
</tr>
</thead>
<tbody>
<tr>
<td>[OH]₀, M</td>
<td>0.001</td>
<td>0.001</td>
<td>0.002</td>
</tr>
<tr>
<td>Initial rate, 1/(M·s)</td>
<td>1.5x10⁻²</td>
<td>2.8x10⁻²</td>
<td>1.4x10⁻²</td>
</tr>
</tbody>
</table>

**Solution methods are integral, half-life and differential. The data won't work to get half-life, or really integral. Thus, differential makes the most sense.**

Therefore, initial rate = $kC_A^{n_A}C_B^{n_B}$ and log rate = log($k$) + $n_A\log C_A + n_B\log C_B$; plotting log (rate) vs log C while holding one of the initial concentrations constant gives n as the slope and log $k + n\log C$ as the intercept. The n and c in the intercept are for the reactant held at constant concentration. From Figure 4, $n_X = 1$, while $n_{OH} = 0.95$. Thus, it is likely that for X+OH, the order of both reactants is 1. Using this gives the rate constant, $k$, as log $k + n_B\log C_B = -3.6778$, with $n_{OH} = 1$ and $C_{OH} = 0.01$ gives log $k = -1.78$, so that $k = 0.0165$.

Doing the same for the Y+OH data gives Figure 5. The order of the reaction with respect to Y is $n_Y = 1$; while the order with respect to OH, $n_{OH} = 0$. The rate constant $k = 2.77$.

What happens when both are in solution depends on the concentration values. The rate constant of Y-OH is 170x the rate constant of X-OH, thus Y will in general react more quickly than X. Examining this as rateY/rateX = $k_YC_Y/(k_XC_XC_{OH}) = 170*C_Y/(C_XC_{OH})$. Thus Y will react more quickly than X, as long $C_Y/(C_X*C_{OH}) > 0.006$. As COH can be related to pH, the final equation for rate shows that as long as $\log(C_Y/C_X) > 2.22pH-14$, then Y reacts faster than X.
Figure 4. Graph of initial rate data for X+OH.

Figure 5. Initial rate data for Y+OH.
5. The flash photolysis of iodine vapor in a large excess of Argon produces iodine atoms, which then recombine by the reaction:

\[ I + I + Ar \rightarrow I_2 + Ar \]

Determine the reaction order with respect to the reactants and the rate constants for the data given below. Given that Argon does not react, is the reaction order what you would expect? Why?

<table>
<thead>
<tr>
<th>[Ar], M</th>
<th>[I₂], M 2 ms</th>
<th>4 ms</th>
<th>6 ms</th>
<th>8 ms</th>
<th>10 ms</th>
</tr>
</thead>
<tbody>
<tr>
<td>2x10⁻³</td>
<td>8.45x10⁻⁶</td>
<td>8.70x10⁻⁶</td>
<td>8.90x10⁻⁶</td>
<td>9.05x10⁻⁶</td>
<td>9.15x10⁻⁶</td>
</tr>
<tr>
<td>4x10⁻³</td>
<td>8.53x10⁻⁶</td>
<td>8.96x10⁻⁶</td>
<td>9.19x10⁻⁶</td>
<td>9.34x10⁻⁶</td>
<td>9.44x10⁻⁶</td>
</tr>
<tr>
<td>6x10⁻³</td>
<td>8.77x10⁻⁶</td>
<td>9.19x10⁻⁶</td>
<td>9.39x10⁻⁶</td>
<td>9.52x10⁻⁶</td>
<td>9.60x10⁻⁶</td>
</tr>
</tbody>
</table>

\([I₂]₀ = 1x10⁻⁵ \text{ M}\) – concentration before flash photolysis

First, the concentration of [I] must be found – \([I(t)] = 2([I₂]₀ - [I₂(t)])\). In general one would expect that the order would equal the molecularity and that \(n_I = 2\) and \(n_{Ar} = 1\). Data is such that integral method makes the most sense. Start with \(n=2\), so that \((1/C - 1/C₀)\) vs. \(t\) would show a linear relationship. Figure 6 shows this graph. As the correlation coefficient \((r^2)\) is very close to 1, the relationship between \((1/C₁ - 1/C₀)\) and time is linear and the reaction is second order in iodine concentration as expected. This uses the isolation method (ie keeping [Ar] constant) to get the order with respect to iodine.

For the Argon, the slope of the graph in Figure 6 is equal to \(k[Ar]^n\). Thus, log (slope) vs. log [Ar] graph in Figure 7 gives the argon reaction order as its slope and the rate constant in the intercept.

Thus, the \(n_I = 2\); the \(n_{Ar} = 1\) and \(k = 2.14x10⁹ \text{ l}^3/(\text{mole}^3 \text{s})\). If the argon were truly unreactive in this reaction, it likely would not be written in the equation. The argon participates by stabilizing the transition state of the iodine recombination reaction by removing some of the heat generated by the exothermic transition state formation. This is related to the collisions between the Ar and the transition state, which is directly proportional to the pressure.
Figure 6. Second order integral plot for iodine recombination data.

Figure 7. Graph of fractional conversion data from which the order with respect to argon is determined.
6. A spherical, uniform size metal oxide was oxidized by oxygen gas at P=0.21 atm. The oxidation process can be described by the shrinking core model and the following reaction:

\[
< MO > + \frac{1}{2} O_2 \rightarrow < MO_2 >
\]

The molecular weights \(<MO>\) and \(<MO_2>\) are 71 and 87 g/mole, respectively, while the densities are 4 and 3 g/ml, respectively. For the data given below for reaction at 773 K, ascertain the limiting step. If the completion time at 973 K was 1 hour, 25 minutes and 22 seconds, how long would completion take at 1173 K?

<table>
<thead>
<tr>
<th>time</th>
<th>Core diameter &lt;MO&gt;, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hours</td>
<td>Minute</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>0</td>
<td>26</td>
</tr>
<tr>
<td>0</td>
<td>43</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>46</td>
</tr>
</tbody>
</table>

To determine the limiting mechanism, the fraction conversion, \(X\), must be determined. \(X=1-(r_c/R)^3\). As the initial core diameter is 1, the data given for core diameter is \(r_c/R\). Converting the time to seconds and plotting \(t/t_{comp}\) vs \(X\) [film diffusion]; \(1 - 3(1-X)^{2/3} + 2(1-X)^{1/3}\) [product layer diffusion]; and \(1-(1-X)^{1/3}\) [chemical reaction] is given in Figure 8 below. As Figure 8 shows, the chemical reaction graph gives a slope of 1 with an intercept of zero – exactly what is expected for the graphing was performed. Therefore, the chemical reaction is the limiting step.

Once the limiting step is known, and assuming this step is limiting at all temperatures of interest, the \(t_{comp}\) values given can be used to determine the \(t_{comp}\) at 1173 K. For chemical reaction control \(t_{comp} = (\rho B^* R)/(k_r C_b)\). First, the values for \(k_r(T)\) for the given data must be determined. Then, \(t_{comp}k_r = a\) constant for all temperatures. From this, \(k_r(T)\) can be found and log \(k_r\) vs. \(1/T\) plotted to find the Arrhenius activation energy. This gives an activation energy of \(E = 5000\) cal/mole. The \(t_{comp}\) at 1173 is found by the ratio of the \(t_{comp}\) values. Thus, \(t_{comp}(1173) = t_{comp}(773)*\exp(-E/(R*1173))/\exp(-E/(R*773)) = 10000\) [seconds] \(*0.040/0.117 = 2926\) seconds or 48 minutes and 46 seconds.
Figure 8. Graph of shrinking core fraction completed functions as a function of normalized time.