Electrochemistry Problems

1) Suppose a galvanic cell was constructed at 25 ºC using a Cu/Cu$^{2+}$ half-cell in which the molar concentration of Cu$^{2+}$ was 1.00 M, and a hydrogen electrode having a partial pressure of H$_2$ equal to 1 atm. The hydrogen electrode dips into a solution of unknown hydrogen ion concentration, and the two half-cells are connected by a salt bridge. The precise value of $E^o$(Cu$^2$/Cu) is +0.3419 V.

a) Derive an equation for the pH of the solution with the unknown hydrogen ion concentration, expressed in terms of $E_{cell}$ and $E^o_{cell}$.

b) If the pH of the solution were 5.15, what would be the observed potential of the cell.

c) If the cell potential were 0.645 V what would be the pH of the solution?

a) The standard reduction potentials are:

- Cu$^{2+}$(aq) + 2 e$^-\rightarrow$ Cu(s) $E^o = +0.3419$ V
- H$^+$(aq) + e$^-\rightarrow \frac{1}{2}$ H$_2$(g) $E^o = +0.000$ V

The reaction with the greater (more positive) reduction potential will be the reduction and the other reaction will run in reverse and be the oxidation.

Balanced Reaction: Cu$^{2+}$(aq) + H$_2$(g) $\rightarrow$ Cu(s) + 2 H$^+$(aq)

Cell Potential: $E^o_{cell} = E^o_{red(red)} - E^o_{red(ox)} = +0.3419 - 0.000$ V = +0.3419 V

The Nernst Equation relates potentials and concentrations.

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln(Q)$$

For the balanced reaction $Q = \frac{[\text{H}^+]^2}{[\text{Cu}^{2+}]}$.

Solid & pure gas phases are ignored.

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln([\text{H}^+]^2/[\text{Cu}^{2+}])$$

$$E_{cell} = E^o_{cell} - (\frac{RT}{nF})\ln([\text{H}^+]^2/[\text{Cu}^{2+}])$$

-$$E_{cell} - E^o_{cell})(nF/RT) = \ln([\text{H}^+]^2/[\text{Cu}^{2+}])$$

$$\exp[-(E_{cell} - E^o_{cell})(nF/RT)] = (\frac{[\text{H}^+]^2}{[\text{Cu}^{2+}]})$$

$$[\text{H}^+] = \sqrt{\exp[-(E_{cell} - E^o_{cell})(nF/RT)]}$$

$$\text{pH} = -\log[\sqrt{\exp[-(E_{cell} - E^o_{cell})(nF/RT)]}]$$

b) $E_{cell} = E^o_{cell} - (\frac{RT}{nF})\ln([\text{H}^+]^2)$

$$[\text{H}^+] = \frac{10^{-\text{pH}}}{10^{-5.15}} = 7.08\times10^{-6} \text{ M}$$

$$E_{cell} = 0.3419 \text{ V} - (8.314 \text{ J/mol-K}\times298\text{K}/(2\times96,485 \text{ C/mol}))\ln((7.08\times10^{-6})^2)$$

$$E_{cell} = 0.6464 \text{ V}$$

c) $\text{pH} = -\log[\sqrt{\exp[-(E_{cell} - E^o_{cell})(nF/RT)]}]$

$$\text{pH} = -\log[\sqrt{\exp[-(0.645V - 0.3419V)(2\times96,485 \text{ C/mol}/(8.314J/mol-K\times298\text{K})])}]$$

$$\text{pH} = 5.13$$
2) Consider the following reversible reaction with the indicated initial concentrations.
What will the ion concentrations be when equilibrium is reached?
\[ \text{Hg}^{2+}(0.25 \text{ M}) + 2 \text{Fe}^{2+}(0.18 \text{ M}) \rightleftharpoons 2 \text{Fe}^{3+}(0.21 \text{ M}) + \text{Hg(\text{liq})} \]

Useful data:
- \( \text{Hg}^{2+} + 2 \text{e}^- \rightarrow \text{Hg(\text{liq})} \quad E^\circ = +0.854 \)
- \( \text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+} \quad E^\circ = +0.771 \)

The reaction with the greater (more positive) reduction potential will be the reduction and the other reaction will run in reverse and be the oxidation.

Cell Potential: \( E^\circ_{\text{cell}} = E^\circ_{\text{red(\text{red})}} - E^\circ_{\text{red(\text{ox})}} = +0.854 - +0.771 \text{ V} = +0.083 \text{ V} \)

\[ K = \exp(-\Delta G^0/RT) = \exp(nFE^\circ_{\text{cell}}/RT) \]

\[ K = \exp(2^*96,485 \text{ C/mol}*0.083 \text{ V}/8.314 \text{ J/mol-K}^*298\text{K}) = \exp(642) = 642 \]

\[ Q_{\text{init}} = 5.4 \quad I \quad 0.25 \text{ M} \quad 0.18 \text{ M} \quad 0.21 \text{ M} \]

\[ \begin{array}{cccc}
\text{C} & \text{-x} & \text{-2x} & +2x \\
\text{E} & 0.25-x & 0.18 - 2x & 0.21 +2x \\
\end{array} \]

\[ -0.105 < x < 0.09 \]

\[ 642 = (0.21 +2x)^2/[((0.25 -x)(0.18 -2x))^2] \]

Solve graphically using EXCEL

\[ x = 0.0733 \]

\[ \begin{array}{cccc}
\text{[Hg}^{2+}] & \text{[Fe}^{2+}] & \text{[Fe}^{3+}] \\
\text{E} & 0.25-x & 0.18 - 2x & 0.21 +2x \\
\text{E} & 0.1767 & 0.0334 & 0.3566 \\
\end{array} \]

\[ Q = 0.3566^2/(0.1767*0.0334^2) = 645 \]

Error of 0.5 % due to round-off.
3) When AgCl(s) is added to a solution of Br\(^{-}\) (aq) this reversible reaction occurs:
AgCl(s) + Br\(^{-}\) (aq) ⇌ AgBr(s) + Cl\(^{-}\) (aq).
If the initial [Br\(^{-}\) (aq)] = 0.4 M what will be the concentration of Br\(^{-}\) (aq) at
equilibrium?

Useful data:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(E^o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl(s) + e(^-) → Ag(s) + Cl(^{-}) (aq)</td>
<td>+0.222</td>
</tr>
<tr>
<td>AgBr(s) + e(^-) → Ag(s) + Br(^{-}) (aq)</td>
<td>+0.071</td>
</tr>
</tbody>
</table>

The reaction with the greater (more positive) reduction potential will be the
reduction and the other reaction will run in reverse and be the oxidation.
Cell Potential: \(E^o_{cell} = E^o_{red(red)} - E^o_{red(ox)} = +0.222 - +0.071\) V = +0.151 V
K = exp(\(-\Delta G^o/RT\)) = exp(nFE^o_{cell}/RT)
K = exp(1*96,485 C/mol*0.151 V/8.314 J/mol-K*298K)
K = exp(5.88) = 358

358 = Q = [Cl\(^{-}\) (aq)]/[Br\(^{-}\) (aq)]

<table>
<thead>
<tr>
<th>Pure solid phases are ignored.</th>
<th>[Cl(^{-}) (aq)]</th>
<th>[Br(^{-}) (aq)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.0</td>
<td>0.4 M</td>
</tr>
<tr>
<td>C</td>
<td>x</td>
<td>-x</td>
</tr>
<tr>
<td>E</td>
<td>x</td>
<td>0.4-x</td>
</tr>
</tbody>
</table>

358 = x/(0.4-x)
143.2 – 358 x = x
143.2 = 359 x
x = 0.3989

E  0.3989 M  0.0011