Electrochemical Cell Potential Calculation **9.24.01. R. Corn**

Consider the electrochemical cell:

$$Ag_{(s)} \mid AgCl_{(s)} \mid Cl^{-} \parallel Zn^{2+} \mid Zn_{(s)}$$

The Cell Potential ε_{cell} can be calculated by two methods:

Method 1: Total Reaction Method

The total cell reaction is:

$$Zn^{2+} + 2Ag_{(s)} + 2Cl^{-} \implies Zn_{(s)} + 2AgCl_{(s)}$$

$$\varepsilon_{cell} = \varepsilon^{\circ}_{cell} - (RT/2F) \ln (1/([Zn^{2+}][Cl^{-}]^{2}) \qquad (1)$$

where $\varepsilon^{\circ}_{cell} = -\Delta G^{\circ}/2F$

Method 2: Half Cell Potential Method

$$\varepsilon_{cell} = E_{Zn} - E_{AgCl} \qquad (2)$$

$$Zn^{2+} + 2e \implies Zn_{(s)}$$

$$E_{Zn} = E^{\circ}_{Zn} - (RT/2F) \ln (1/[Zn^{2+}]) \qquad (3)$$

$$AgCl_{(s)} + e \implies Ag_{(s)} + Cl^{-}$$

$$E_{AgCl} = E^{\circ}_{AgCl} - (RT/F) \ln ([Cl^{-}]) \qquad (4)$$

Equivalence of the Two Methods

Now since $(RT/F) \ln ([Cl^{-}]) = -(RT/F) \ln (1/[Cl^{-}]) = -(RT/2F) \ln (1/[Cl^{-}]^{2})$
this eqn becomes:

$$E_{AgCl} = E^{\circ}_{AgCl} + (RT/2F) \ln (1/[Cl^{-}]^{2}) \qquad (5)$$

$$\varepsilon_{cell} = (E^{\circ}_{Zn} - (RT/2F) \ln (1/[Zn^{2+}])) - (E^{\circ}_{AgCl} + (RT/2F) \ln (1/[Cl^{-}]^{2})) \qquad (6)$$

$$\varepsilon_{cell} = (E^{\circ}_{Zn} - E^{\circ}_{AgCl}) - (RT/2F) \ln (1/([Zn^{2+}][Cl^{-}]^{2}) \qquad (7)$$

If we define $(E^{\circ}_{Zn} - E^{\circ}_{AgCl}) = \varepsilon^{\circ}_{cell}$, Then we see that this is exactly the same equation that we found by Method 1 (Equation 1).