

Electrochemical Cell Potential Calculation

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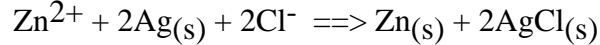
Consider the electrochemical cell:



The Cell Potential $\mathcal{E}_{\text{cell}}$ can be calculated by two methods:

Method 1: Total Reaction Method

The total cell reaction is:

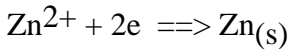


$$\mathcal{E}_{\text{cell}} = \mathcal{E}^{\circ}_{\text{cell}} - (RT/2F) \ln (1/([\text{Zn}^{2+}][\text{Cl}^-]^2)) \quad (1)$$

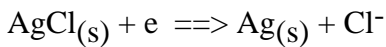
where $\mathcal{E}^{\circ}_{\text{cell}} = -\Delta G^{\circ}/2F$

Method 2: Half Cell Potential Method

$$\mathcal{E}_{\text{cell}} = E_{\text{Zn}} - E_{\text{AgCl}} \quad (2)$$



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



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

Equivalence of the Two Methods

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

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

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

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

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