METAL INDICATOR ELECTRODES

SDSU CHEM 251

METAL INDICATOR ELECTRODES

- Metal indicator electrodes are systems that use specific metal electrodes as the indicator electrode in an electrochemical measurement.
- $E_{cell} = E_{ind} - E_{ref} + E_j$
- These indicator electrodes are paired with a reference electrode (e.g. SHE, SCE, Ag/AgCl) and can be used to determine the concentrations of targeted analytes in a solution. The cell potential will be directly influenced by the target analyte concentration.

KINDS OF METAL INDICATOR ELECTRODES

- There are two kinds of metal indicator electrodes:

- **Electrodes of the first kind**: where the electrode potential responds directly in relationship to the concentration of the metal ion of interest.

    - Cu^{2+}, with a $Cu_{(s)}$ electrode; $Cu^{2+} + 2e^{-} \rightleftharpoons Cu_{(s)}$

- **Electrodes of the second kind**: where the metal ion is in equilibrium with the target analyte, that equilibrium influences the availability of the metal ion to interact with the electrode.

    - $Cu^{2+} + 2I^{-} \rightleftharpoons CuI_{2(s)}$ with the above electrode system.

METAL INDICATOR ELECTRODES OF THE FIRST KIND

- Require a pure metal of that analyte that can be used as the indicator electrode. There are a limited number of metals appropriate for such reactions (Ag, Bi, Cd, Cu, Hg, Pb, Sn, Ti & Zn).

- Due to the simplicity of the redox reaction the potential for such cells can be reduced to a simple equation containing a single constant and dependent on the concentration of the metal ion.

$$Cu^{2+} + 2e^{-} \Leftrightarrow Cu_{(s)}$$

$$E_{cell} = E_{ind} - E_{ref} + E_j$$

$$E_{ind} = E^\circ - \frac{0.05916}{n} \log \frac{1}{\left[Cu^{2+}\right]}$$

$$E_{cell} = E^\circ - \frac{0.05916}{n} \log \frac{1}{\left[Cu^{2+}\right]} - E_{ref} + E_j$$

Constants: E°, E_{ref}, E_j Let: $K = E^\circ - E_{ref} + E_j$

$$E_{cell} = K - \frac{0.05916}{n} \log \frac{1}{\left[Cu^{2+}\right]}$$

$$E_{cell} = K + \frac{0.05916}{n} \log \left[Cu^{2+}\right]$$

METAL INDICATOR ELECTRODES OF THE FIRST KIND

$$E_{cell} = K + \frac{0.05916}{n} \log\left[Cu^{2+}\right]$$

- In order to use an electrode of the first kind, one would first need to calibrate the instrument with known concentrations of the metal ion (e.g. Cu^{2+}) in order to determine the value of the constant (*K*).

- With the constant determined unknown solutions containing that metal ion could be measured and the cell potential directly converted to a concentration.

METAL INDICATOR ELECTRODES OF THE SECOND KIND

- The electrodes that can be used as electrodes of the first kind can also be used to determine the concentration of other species in solution, provided that the metal ions interact with this new analyte.

- These are termed electrodes of the second kind, if there is an equilibrium between the metal ion and the analyte the potential for the cell can be expressed in terms of that analyte.

- The S.C.E. and Ag/AgCl reference electrodes are electrodes of the second kind.

METAL INDICATOR ELECTRODES OF THE SECOND KING

$$E_{cell} = E_{ind} - E_{ref} + E_j$$

$$Cu^{2+} + 2I^- \Leftrightarrow CuI_{2(s)} \quad K_{sp} = \left[Cu^{2+}\right]\left[I^-\right]^2 \quad \left[Cu^{2+}\right] = \frac{K_{sp}}{\left[I^-\right]^2}$$

$$E_{ind} = E^\circ - \frac{0.05916}{n}\log\frac{1}{\left[Cu^{2+}\right]} \quad E_{ind} = E^\circ - \frac{0.05916}{n}\log\frac{1}{\frac{K_{sp}}{\left[I^-\right]^2}} \quad E_{ind} = E^\circ - \frac{0.05916}{n}\log\frac{\left[I^-\right]^2}{K_{sp}}$$

$E_{ref}, E^\circ, E_j, K_{sp}$ are all constants $\quad \log\frac{x}{y} = \log x - \log y \quad$ Let: $K = E^\circ - E_{ref} + E_j + \frac{0.05916}{n}\log\left(K_{sp}\right)$

$$E_{cell} = K - \frac{0.05916}{n}\log\left[I^-\right]^2$$

n = electrons involved in metal indicator electrode redox reaction.

METAL INDICATOR ELECTRODES OF THE SECOND KIND

$$E_{cell} = K - \frac{0.05916}{n}\log\left[I^-\right]^2 \quad E_{cell} = K' - \frac{0.05916}{n}\log\frac{\left[I^-\right]^2}{K_{sp}}$$

- There are several ways that a metal indicator electrode of the second kind can be used to quantify an interacting ion.
- In all cases the original concentration of the metal ion needs to be known prior to the analysis.
- Uses of these electrodes include titrations, and direct analysis of analyte solutions.