MEMBRANE ION SELECTIVE ELECTRODES

SDSU CHEM 251
MEMBRANE ELECTRODES

• Membrane electrodes were first discovered in 1901, by Fritz Haber.

• He found that placing a glass membrane between two solutions of different pH changed the potential of the membrane.

• This membrane potential led to the proliferation of potentiometric methods beyond the metallic indicator electrodes - resulting in modern ion-selective electrodes.
SELECTIVE MEMBRANES

• The goal for selective membranes is to limit the analytes that can pass through/interact with the membrane.

• This allows for a very complex sample to be measured more effectively - reducing potential for errors in measurement due to complex matrices.

• Extensive research effort is placed in developing new membranes with greater/different selectivities.
MEMBRANE POTENTIAL

A membrane potential is developed in ion-selective electrodes (ISE) due to the differences in the activity of the analyte on either side of the membrane.

The system consists of two reference electrodes which have constant potentials, as does the junction potential.

Changes in the cell potential are due solely to the membrane potential.

\[ E_{\text{cell}} = E_{\text{ref(int)}} - E_{\text{ref(samp)}} + E_{\text{mem}} + E_{\text{j}} \]

\( \text{reference(sample) } \| [A]_{\text{samp}}(aq, a_A = x) \| [A]_{\text{int}}(aq, a_A = y) \| \text{reference(internal)} \)
MEMBRANE POTENTIAL

- Current is carried through the membrane either by the analyte ion or a specialized ion already present in the membrane.

- As the membrane potential is proportional to the activity difference of the analytes on either side the cell potential can be expressed as a function of this ratio.

- Since the concentration of the analyte within the ISE is constant the equation can be further simplified to be proportional to the the activity of the analyte in the sample.

$$E_{cell} = E_{ref\,(int)} - E_{ref\,(samp)} + E_j + E_{mem}$$

$$E_{mem} = E_{asym} - \frac{RT}{zF} \ln \frac{[A]_{int}}{[A]_{samp}}$$

Constants: $E_{ref\,(int)}, E_{ref\,(samp)}, E_j, E_{asym}, R, T, F, [A]_{int}$

$$E_{cell} = K + \frac{0.05916}{z} \log[A]_{samp}$$

$z$: charge of analyte (includes magnitude and sign)
MEMBRANE SELECTIVITY

• The desire with ISE membranes if for perfect selectivity - a membrane that responds only to a single analyte.

• The reality is that, due to the fact that they rely on chemical interactions, selective membranes can interact with chemicals similar to their desired analytes.

• Consequently, the presence of other components in the solution that are similar to the analyte, the measured potential may not accurately reflect the concentration of the analyte.
SELECTIVITY COEFFICIENT

- The effect of the membrane responding to interferents is additive - it increases the potential above that from the analyte.

- The magnitude of the response of a selective membrane to an interferent can be quantified in terms of the selectivity coefficient \( K_{A,I} \).

- The interference is also related to the ratio of the charges of the analyte \( z_A \) and interferent \( z_I \).

\[
E_{cell} = K + \frac{0.05916}{z_A} \log \left\{ [A]_{samp} + K_{A,I} \left[ I \right]^{\frac{z_A}{z_I}} \right\}
\]

\[
K_{A,I} = \frac{[A]_{samp}}{[I]^{\frac{z_A}{z_I}}}
\]

If \( K_{A,I} = 1 \) there is no selectivity between the analyte (A) and interferent (I), membranes with good selectivities have values of \( K_{A,I} \) well below 1.
SELECTIVITY COEFFICIENT

• $K_{A,I}$ is defined as the ratio of the concentrations of A and I that will yield the same potential with the membrane.

• The $K_{A,I}$ can be determined through analysis of the cell potential.

• The selectivity coefficients for most commercially available ion-selective electrodes are provided by the manufacturers.

The intersection of the two linear lines is the concentration of A that yields a potential equal to that of I at its given concentration.