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

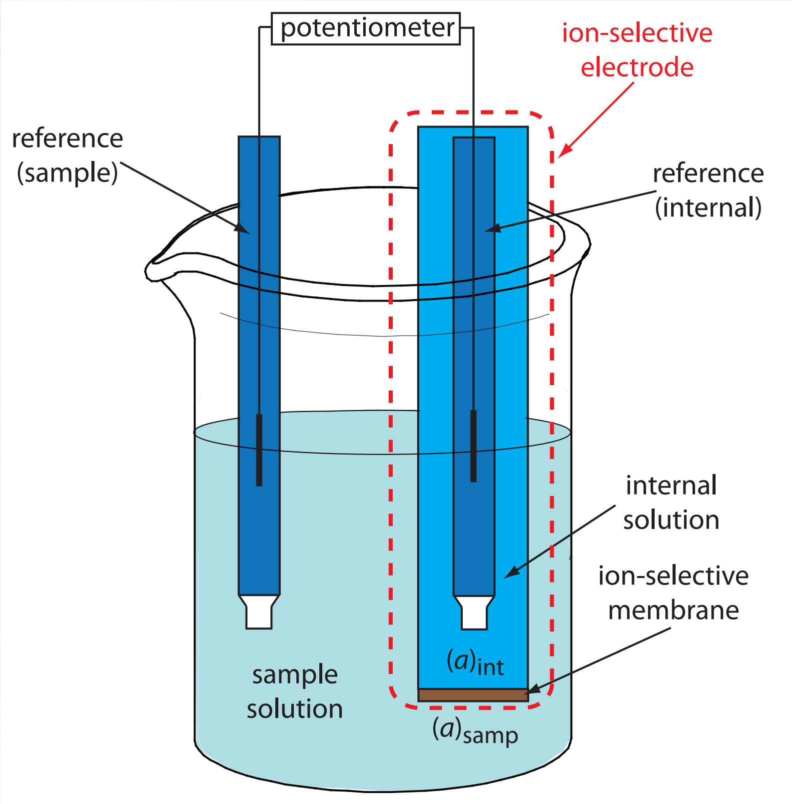
- The goal for selective membranes is to limit the analytes that can pass through/interact with the membrane.
- This allows for a very complex sample to be measured more effectively - reducing potential for errors in measurement due to complex matrices.
- Extensive research effort is placed in developing 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.



$$E_{cell} = E_{ref(int)} - E_{ref(samp)} + E_{mem} + E_{j}$$

$$\text{reference(sample)} \,\|\, [\mathrm{A}]_{samp}(aq, a_{\mathrm{A}} = x) \,|\, [\mathrm{A}]_{int}(aq, a_{\mathrm{A}} = y) \,\|\, \text{reference(internal)}$$

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.

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

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

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

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

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).

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

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

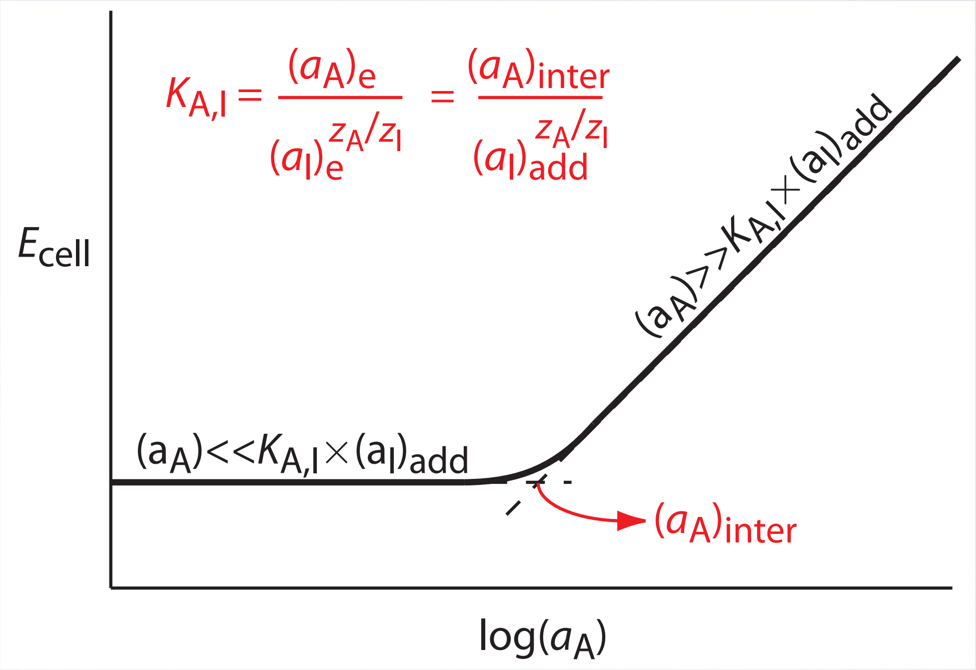
If $K_{A,I} = 1$ there is no selectivity between the analyte (A) and interferent (I), membranes with good selectivities have values of $K_{A,I}$ well below 1.

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 it's given concentration.