ELECTROCHEMICAL MEASUREMENT BASICS

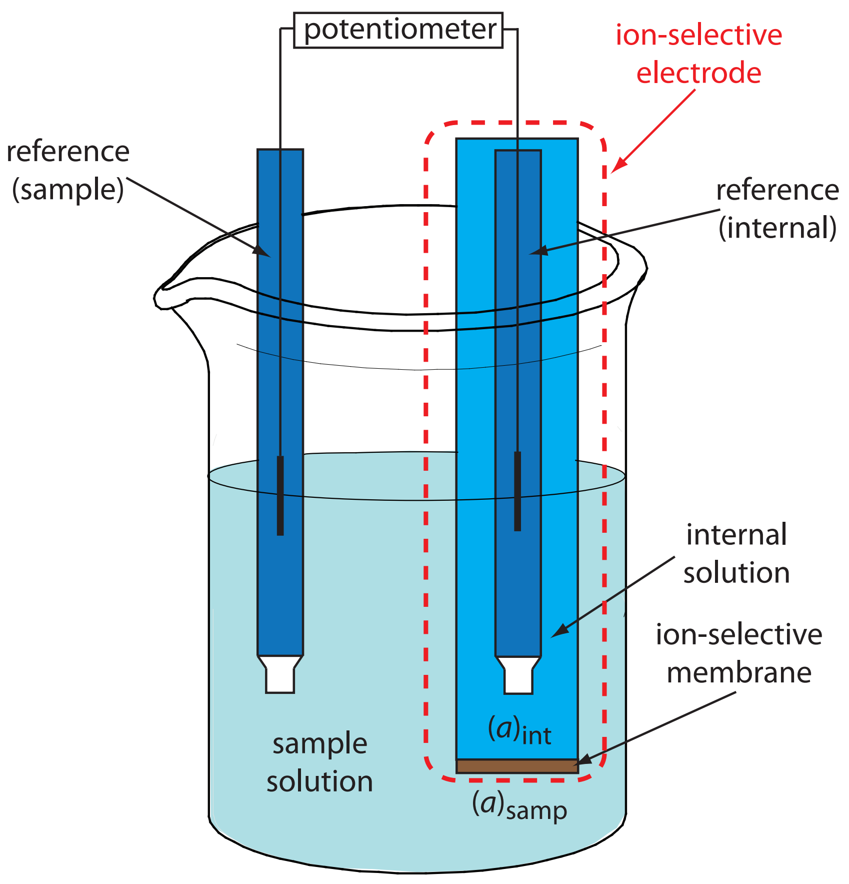
SDSU CHEM 251

ELECTROCHEMICAL ANALYSES

- Electrochemical analyses rely on the movement of electrons in redox reactions to provide the means of quantifying an analyte in solution.
- Quantification can be based on the measurement of the cell's potential, charge, or current.
- Our focus will be on potentiometric systems, where the cell potential is measured to determine the analyte concentration.

ELECTROCHEMICAL CELLS

- Measurements of solutions by potentiometry is much like what was done for redox titrations.
- The potential is measured between a selective electrode and a reference electrode.
- The potential due to the selective electrode is proportional to the concentration of the analyte of interest.



ELECTROCHEMICAL MEASUREMENTS

- In potentiometry the Nernst equation can be applied directly to the analysis.

- By convention the **reference electrode** is always the **anode** and the **indicator electrode** the **cathode**.

- Potentiometry systems are typically designed in such a way that the indicator signal is dependent solely on the one species of interest.

$$E = E_{cathode} - E_{anode}$$

$$E = E_{ind.} - E_{ref.}$$

$$E_{ind.} = E^{0} - \frac{0.05916}{n} \log \frac{[prod]}{[react]}$$

IMPACTS OF DIFFUSION

- As the measurement of the analyte of interest only occurs at the surface of the electrode (not in the bulk of the solution) getting the analyte to the electrode is important.

- If only diffusion is used to get the analytes to the electrode surface this can result in errors/problems in measurements.

- This can be overcome to a large extent by stirring the solution.

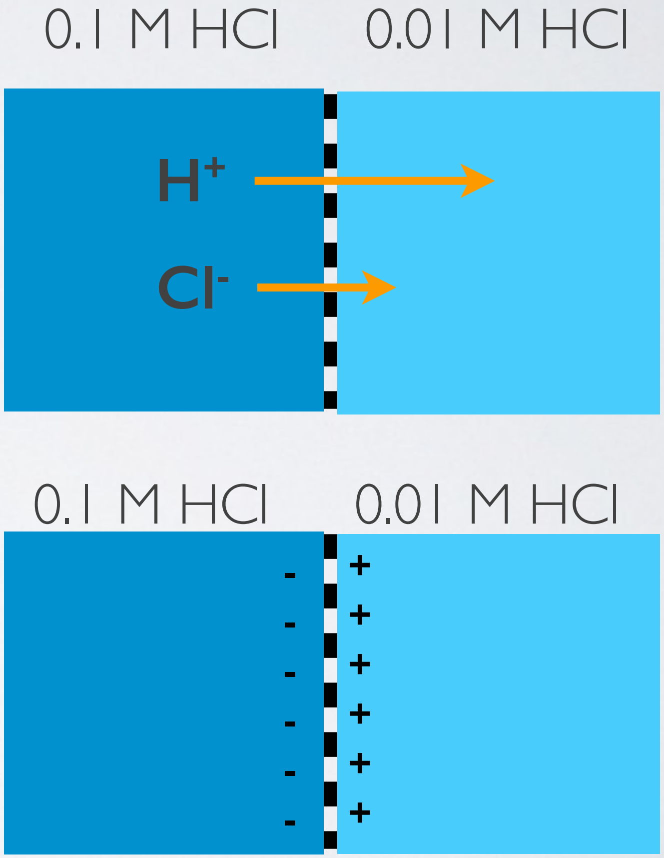
- However, the diffusion of ions through the porous membrane of the salt bridge cannot be compensated for by stirring and as a result, this will have an impact on the measurements.

JUNCTION POTENTIAL

- Junction potentials arise when ions diffuse across porous membranes at different rates, such as the porous membranes of salt bridges.

- The consequence is a charge difference on either side of the membrane - a potential (30-40 mV) that will contribute to any measurements of cell potential.

- Use of KCl minimizes this as the diffusion rates of K^+ and Cl^- are comparable.



JUNCTION POTENTIALS

- We have assumed that there is no junction potential in our cell calculations ($E_{cell} = E_+ - E_-$).
- The reality is that a junction potential exists and need to be compensated for in cell measurements ($E_{cell} = E_+ - E_- + E_j$).
- The value of E_j is typically unknown, but with proper calibration/standardization it does not need to be measured in order to perform accurate quantitative work.