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.

Figure 11.14: Schematic diagram showing a typical potentiometric cell with an ion-selective electrode.
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.

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E = E_{\text{cathode}} - E_{\text{anode}}
\]

\[
E = E_{\text{ind.}} - E_{\text{ref.}}
\]

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