The silver-silver chloride electrode (SSCE) is one of the most commonly used reference electrodes.

- It is typically constructed as a thin tube that is subsequently dipped into solution.

Silver-Silver Chloride Reference Electrode

salt bridge

Ag

AgCl saturated KCl solution

solid KCl

Fe²⁺

Fe³⁺

Pt

Anode: Ag + Cl⁻ ⇌ AgCl + e⁻

Cathode: Fe³⁺ + e⁻ ⇌ Fe²⁺

_____
Electrode

Part of the cell that is held constant.

_____
Electrode

Part of the cell that contains the analyte being analyzed.
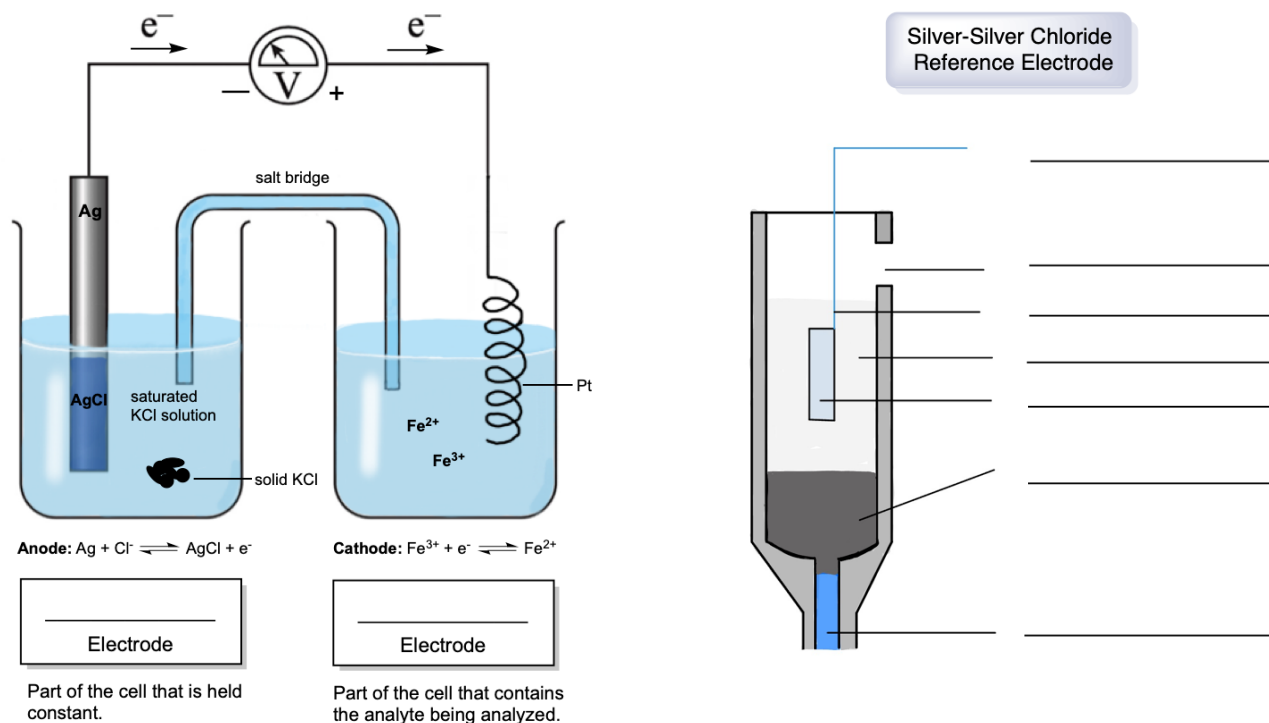
When the chloride concentration approaches unity the standard cell potential is 0.222 V.

- This reference electrode is based on the redox couple between AgCl and Ag.
- The activity of the chloride ion determines the potential of the electrode.

$$AgCl\,(s) \;+\; e^- \;\rightleftharpoons\; Ag\,(s) \;+\; Cl^- \qquad E^\circ = 0.222\ V$$
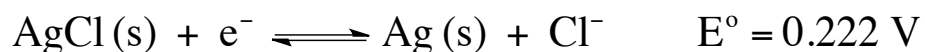
When dealing with a saturated solution of KCl the new standard cell potential becomes _____ at 25 °C, and when dipped into 3.5 M KCl the new standard cell potential becomes _____ at 25 °C.

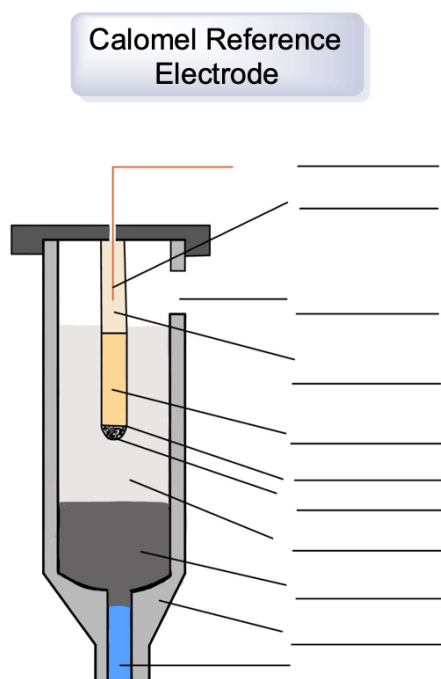The electrode's cell notation can be written as:

$$Ag\,(s)\,\big|\,AgCl\,(s)\,,\,KCl\,(aq,\ a_{Cl^-} = x)\big\|$$
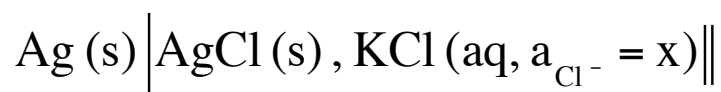
<u>**CONCEPT:**</u> <u>SATURATED CALOMEL REFERENCE ELECTRODE</u>

The calomel reference electrode is based on the following redox couple reaction between Hg_2Cl_2 and Hg.

$$Hg_2Cl_2 \text{ (s)} + 2\text{ e}^- \rightleftharpoons 2\text{ Hg (l)} + 2\text{ Cl}^- \text{ (aq)}$$
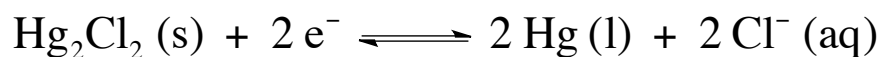
The Saturated Calomel Reference Electrode is commonly referred to as S.C.E.

Calomel Reference Electrode

Using the Nernst equation we obtain:

$$E = E^0_{Hg_2Cl_2/Hg} - \frac{0.05916\text{ V}}{n}\log(a_{Cl^-})^2 = +0.268\text{ V} - \frac{0.05916\text{ V}}{2}\log(a_{Cl^-})^2$$

From the equation it is determined that the potential of the electrode is based on the activity of the chloride ion.

- The concentration of the chloride ion is determined by the solubility of KCl.

- The potential is 0.268 V when the activity of the chloride ion approaches unity.

- When the concentration of KCl is 0.100 M or 1.00 M the potential is _____ or _____ respectively.

- The potential can also be affected by temperature: at 25 ºC it is _____ and at 35 ºC it is _____. The electrode's cell notation can be written as:

$$Hg \text{ (l)} \left| Hg_2Cl_2 \text{ (s)}, KCl \text{ (aq, saturated)} \right\|$$