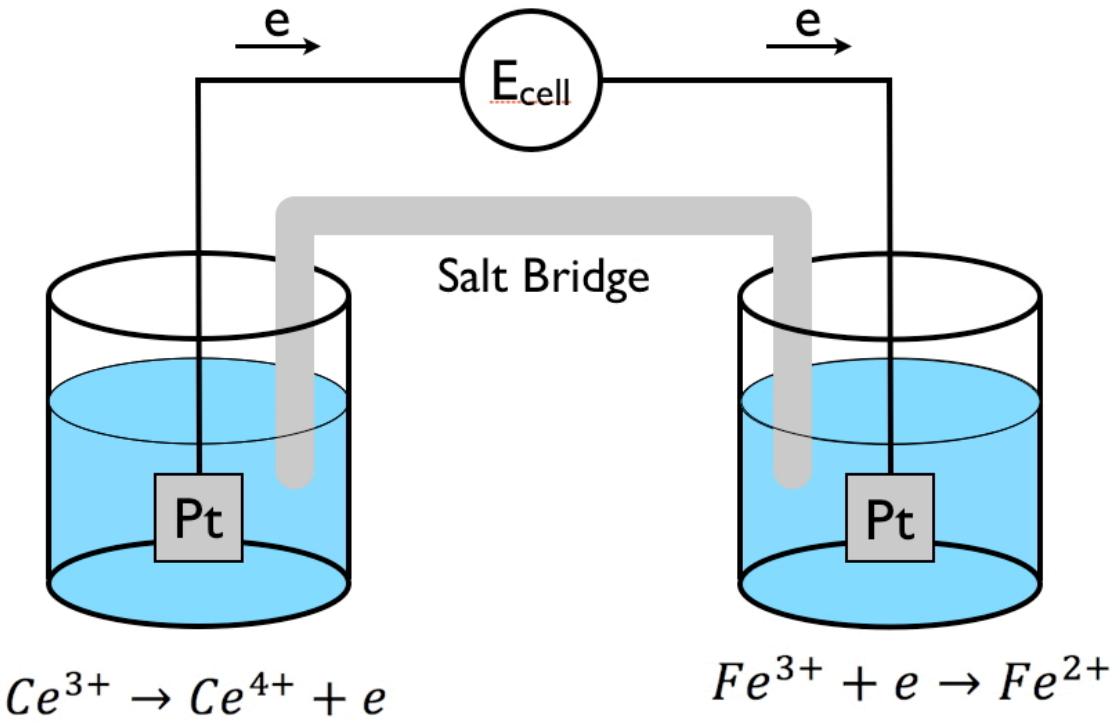
Potentiometry

$Ce^{3+} \rightarrow Ce^{4+} + e$

Oxidation

$Fe^{3+} + e \rightarrow Fe^{2+}$

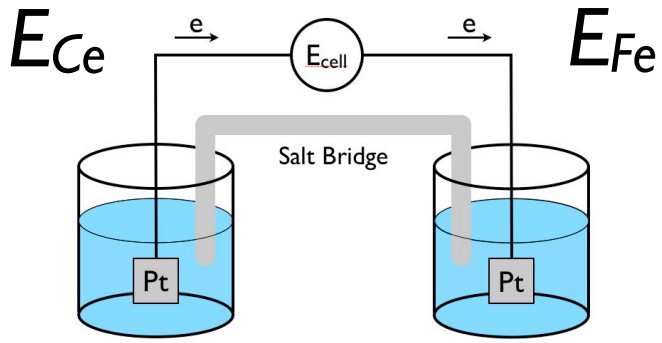
Reduction



R. Corn Fall 2012

Half Cell Potentials

$$E_{cell} = E_{Fe} - E_{Ce}$$



Half Cell Potentials are always written as reductions:

$$Fe^{3+} + e \rightarrow Fe^{2+}$$

$$E_{Fe} = E^0_{Fe} - \frac{RT}{F} ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$Ce^{4+} + e \rightarrow Ce^{3+}$$

$$E_{Ce} = E^0_{Ce} - \frac{RT}{F} ln \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$E_{cell} = E_{red} - E_{ox}$$

$$E_{cell} = E_{red} - E_{ox}$$

Since we always use half cell differences, we can add an arbitrary constant to all half cells. By convention, we assume that the E^o for the normal hydrogen electrode (NHE) is equal to zero:

Half Cell Reaction for Hydrogen:

$$H^+ + e \rightarrow \frac{1}{2} H_{2(g)}$$

$$E_H = E_H^0 + \frac{RT}{F} ln \frac{{P_{H_2}}^{1/2}}{[H^+]} \qquad E_H^0 = 0$$

Other Types of Electrodes

Metal Indicator Electrodes

$$Ag^+ + e \rightarrow Ag_{(s)}$$

$$E_{Ag} = E^0_{Ag} - \frac{RT}{F} ln \frac{1}{[Ag^+]}$$

Silver Electrode:
Used to measure
[Ag+] in solutions

Reference Electrodes

$$AgCl_{(s)} + e \rightarrow Ag_{(s)} + Cl^-$$

$$E_{AgCl} = E^0_{AgCl} - \frac{RT}{F} ln \frac{[Cl^-]}{1}$$

Silver Chloride
Reference Electrode:
Only depends on [Cl-]

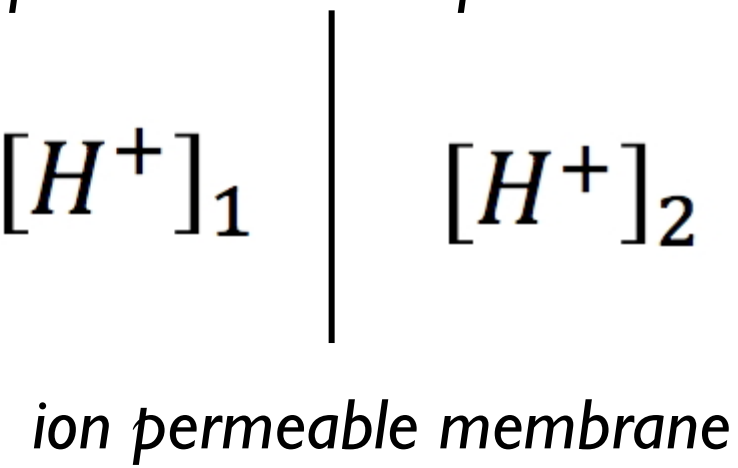
Other Types of Electrodes

Membrane and Ion Selective Electrodes (ISEs)

$$E_{cell} = E_{red} - E_{ox} + E_j$$

E_j is a junction potential that is sensitive to only one ion:

$$E_j = -\frac{RT}{F} ln \frac{[H^+]_1}{[H^+]_2}$$



E_{red} and E_{red} are typically both references electrodes (e.g., AgCl)

Other Types of Electrodes

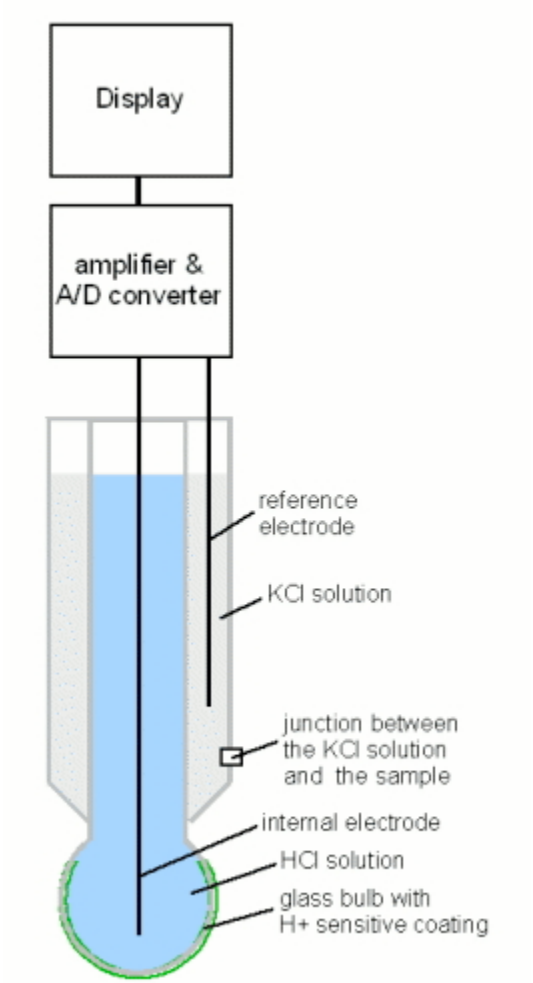
Membrane and Ion Selective Electrodes (ISEs)

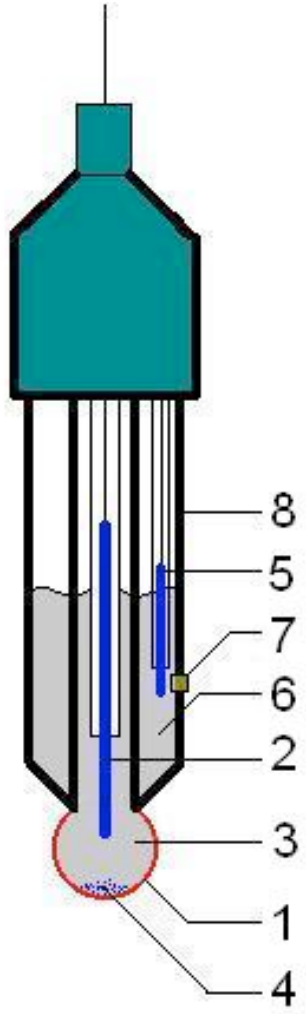
pH Electrode

Ca^{2+} Electrode

NO_3^- Electrode

Corning glass membrane





Other Types of Electrodes

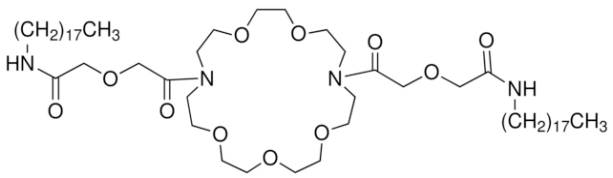
Membrane and Ion Selective Electrodes (ISEs)

pH Electrode

Ca^{2+} Electrode

NO_3^- Electrode

Polymer (PVC)membrane electrode containing a calcium ionophore



Specifications

- Range: 0.20 to 40,000 mg/L or ppm (5×10^{-6} M to 1.0 M)
- Resolution (LabQuest 2, LabQuest, LabQuest Mini, Go!Link, LabPro):
  - % of reading: 1.4%
  - Low scale reading: 0.20 ±0.0028
  - High scale reading: 40,000 ±560 mg/L
- pH Range: 3 to 10
- Interfering Ions: Pb^{2+}, Hg^{2+}, Sr^{2+}, Cu^{2+}, Ni^{2+}
- Electrode Resistance: 1 to 4 MΩ
- Electrode Slope (log voltage vs. concentration): +28 mV/decade
- Reproducibility: ± 5% of reading
- Temperature range (can be placed in): 0 to 50°C (no temperature compensation)
- Minimum immersion: 1 inch
- Electrode Length: 155 mm
- Body Diameter: 12 mm
- Cap Diameter: 16 mm
- Cable Length: 100 cm

Other Types of Electrodes

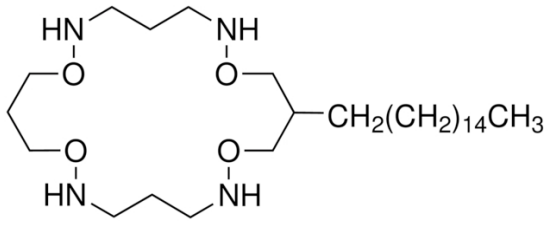
Membrane and Ion Selective Electrodes (ISEs)

pH Electrode

Ca^{2+} Electrode

NO_3^- Electrode

Polymer (PVC)membrane electrode containing a nitrate ionophore



Specifications

- Range: 0.10 to 14,000 mg/L or ppm (7×10^{-6} M to 1.0 M)
- Resolution (LabQuest 2, LabQuest, LabQuest Mini, GoILink, LabPro):
  - % of reading: 0.7%
  - Low scale reading: 0.10 ±0.0007
  - High scale reading: 14,000 ±98 mg/L
- pH Range: 2.5 to 11
- Interfering Ions: ClO_4^-, I^-, ClO_3^-, CN^-, BF_4^-
- Electrode Slope (log voltage vs. concentration): –56 mV/decade
- Electrode Resistance: 1 to 4 MΩ
- Reproducibility: ± 5% of reading
- Temperature range (can be placed in): 0 to 50°C (no temperature compensation)
- Minimum immersion: 1 inch
- Electrode Length: 155 mm
- Body Diameter: 12 mm
- Cap Diameter: 16 mm
- Cable Length: 100 cm