REDOX TITRATION POTENTIAL MEASUREMENTS

SDSU CHEM 251

REDOX TITRATION

- A redox titration is the controlled addition of one of the redox reagents to the other.
- The redox titration can oxidize or reduce the analyte.
- The titrant must be reduced or oxidized in turn.
- The reaction should be fast and proceed to completion upon mixing.

Analyte: A^+ Titrant: T^{3+}

Oxidation: $A^+ \rightleftharpoons 2e^- + A^{3+}$ Reduction: $T^{3+} + e^- \rightleftharpoons T^{2+}$

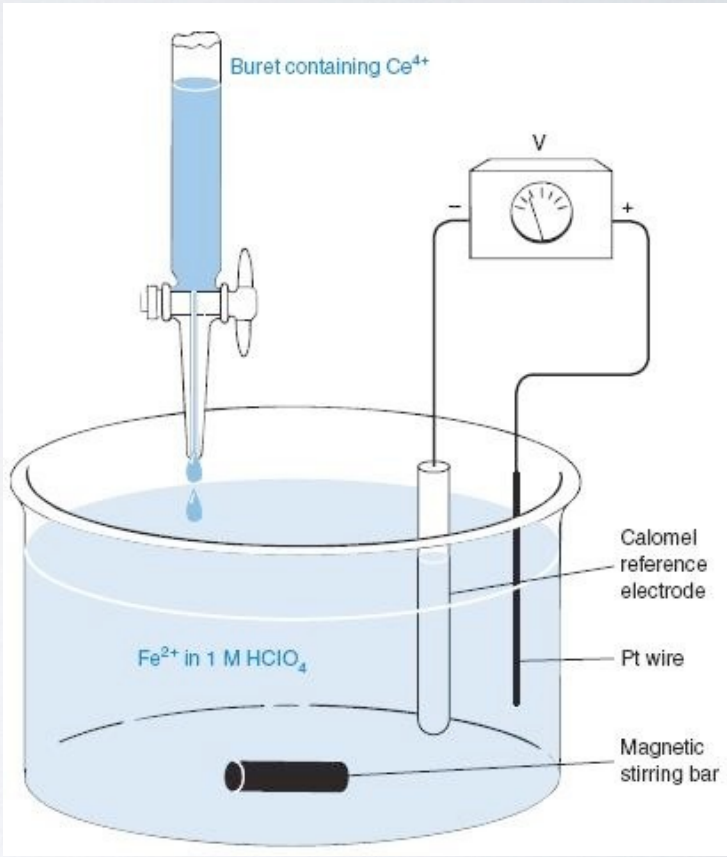
Net Reaction: $A^+ + 2T^{3+} \rightleftharpoons A^{3+} + 2T^{2+}$

HALF REACTION POTENTIAL

- As the analyte and titrant are mixed there is a transfer of electrons through the REDOX reaction.
- Once this transfer is completed (a rapid reaction) the system is at equilibrium and no potential can be measured ($E_{cell} = 0\,V$).
- At equilibrium, if the potential is measured for either the reduction or oxidation half reactions, it would be the same, since $\mathbf{E_{cell} = E_{+} - E_{-}}$ thus: $\mathbf{E_{+} = E_{-}}$.

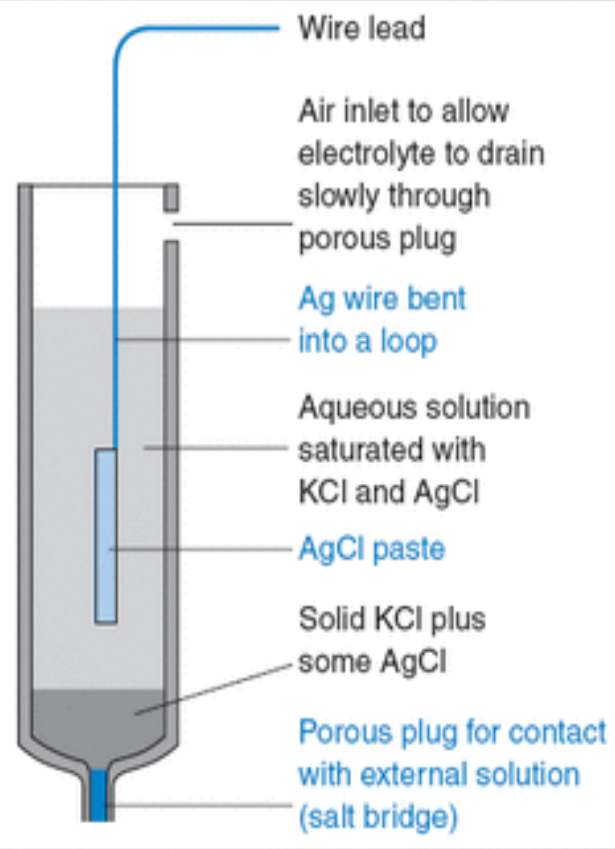
MEASURING REACTION PROGRESS

- As the titration reaches an equilibrium (E_{cell} = 0V) after each addition of titrant, the determination of the extent of the reaction progress requires an external probe.
- A standard reference electrode (a half-cell) is inserted into the flask to act as a reference potential ($\mathbf{E_{ref}}$).
- This potential is measured against the potential of the analyte (or titrant) half reaction to give a whole cell potential: $\mathbf{E_{cell} = E_{+/-} - E_{ref}}$.



REFERENCE ELECTRODES

- Reference electrodes are designed to act as half of the galvanic cell (plus the salt bridge).
- They are self contained and maintain a constant potential.
- Reference cells can be inserted into almost any solution.
- Common reference cells are:
- Saturated calomel electrode (SCE = 0.241 V).
- Saturated silver - silver chloride cells (0.197 V)



CALCULATION

$$IrCl_6^{2-} + e^- \rightleftharpoons IrCl_6^{3-} \quad E° = 1.026\,V$$

What would be the potential of a cell containing 5.23 mM $IrCl_6^{2-}$ and 10.9 mM $IrCl_6^{3-}$ measured against:

a) A saturated Ag/AgCl electrode?
b) A SCE?