

REDOX TITRATION CALCULATIONS

SDSU CHEM 251

CALCULATING POTENTIAL

- The cell potential for the solution will depend on the conc. of the analyte (or titrant) in each oxidation state.
- As the titration progresses the concentrations will change, altering the potential.
- Three distinct situation arise for the calculations.
- By convention the reference electrode is taken to be E_- (anode) , the titration cell is E_+ (cathode).

SAMPLE PROBLEM

A 15 mL solution of Ru^{2+} (40 mM) can be oxidized by reaction with Au^{3+} . A titration is performed with a saturated calomel reference electrode (S.C.E.) as the anode and a platinum wire as a cathode. Determine the cell potential at various titration volumes, below, if the titrant is made of 12 mM Au^{3+} .

What would be the cell potential at the following titration volumes:

- a) 15.00 mL
- b) 25.00 mL
- c) 32.53 mL

BEFORE THE EQUIVALENCE POINT

- The cell potential is not calculated before the titrant is added.
- As titrant is added the concentration of the analyte product increases.
- Knowing the conc. of the analyte in both oxidation states we can calculate E_+ for the cell and thus E_{cell} .
- At $V = \frac{1}{2} V_{\text{eq}}$ $E_+ = E^\circ$
- Calculation can be done for the titrant species, we get the same E_{cell} , but it is much more difficult.

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AT THE EQUIVALENCE POINT

- When we reach the equivalence point all the analyte has been reacted with titrant.
- But some reverse reaction occurs - both analyte and titrant undergo some back-reaction: $A^+ + 2T^{3+} \rightleftharpoons A^{3+} + 2T^{2+}$
- Calculation for E_+ is based on both half-reactions (weighted by their number of e^-).

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AFTER THE EQUIVALENCE POINT

- Past V_{eq} the analyte has been fully reacted and there is an excess of titrant.
- At this point we know the concentrations of the titrant better than those of the analyte.
- We will use the half-reaction of the titrant species to determine E_{cell}
- At $V = 2V_{eq}$ $E_+ = E^\circ$ (for the titrant)

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