

## Redox Titrations: Electrochemistry Stoichiometry in Action!

**Important Caveat:** at this point in time, we have only performed and analyzed acid-base titrations, but a redox titration is NOT an **ACID-BASE** titration. Although much of our language and calculations will be the same, please be cognizant of the difference and **DO NOT** use acid-base terminology (especially in your lab report ☺).

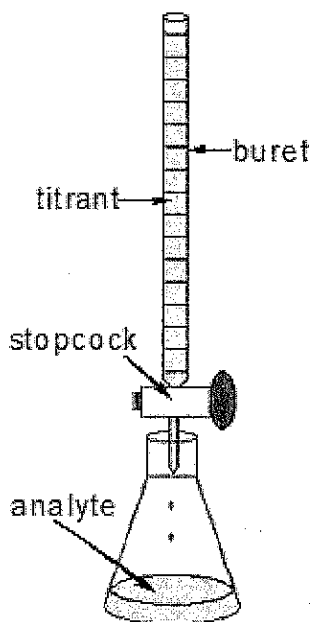
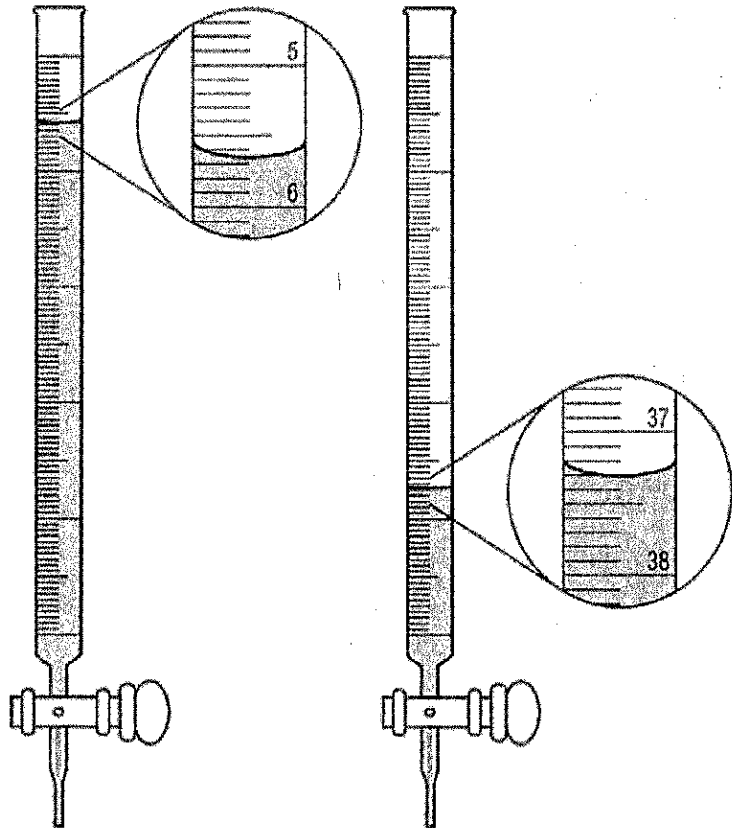


Figure 1: Titration Setup

**Goal of Titration:** determine the unknown concentration of the analyte!

A substance in a solution of Known concentration (the titrant, usually in a buret) is reacted with another substance in a solution of unknown concentration (the analyte, usually in a flask or beaker)

- **Equivalence point:** the point at which the moles of each reactant are **stoichiometrically equal** to each other in solution. (However, this is NOT where the two reactants have neutralized each other: that only happens in an acid-base titration!)
- **End point:** the point of the titration where an indicator changes color (if thoughtfully chosen, this occurs approximately at the equivalence point as a visual indication of the point at which the stoichiometric equivalent has been added).



### Quick Reminder: How to Read a Buret

Burets, unlike most glassware used for precise volume measurements, are read from the top down, not the bottom up!

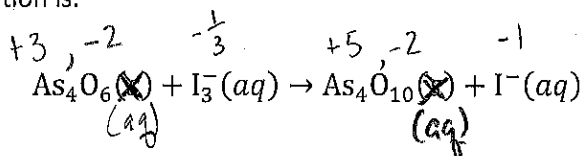
*Example:* The image to the left shows a buret of  $\text{KMnO}_4$  before titration begins (leftmost) and at the end point (rightmost).

1. What volume of solution was initially present in the buret? 5.65 mL
2. What volume was present at the end point of the titration? 37.30 mL
3. How much  $\text{KMnO}_4$  solution was added to the flask?

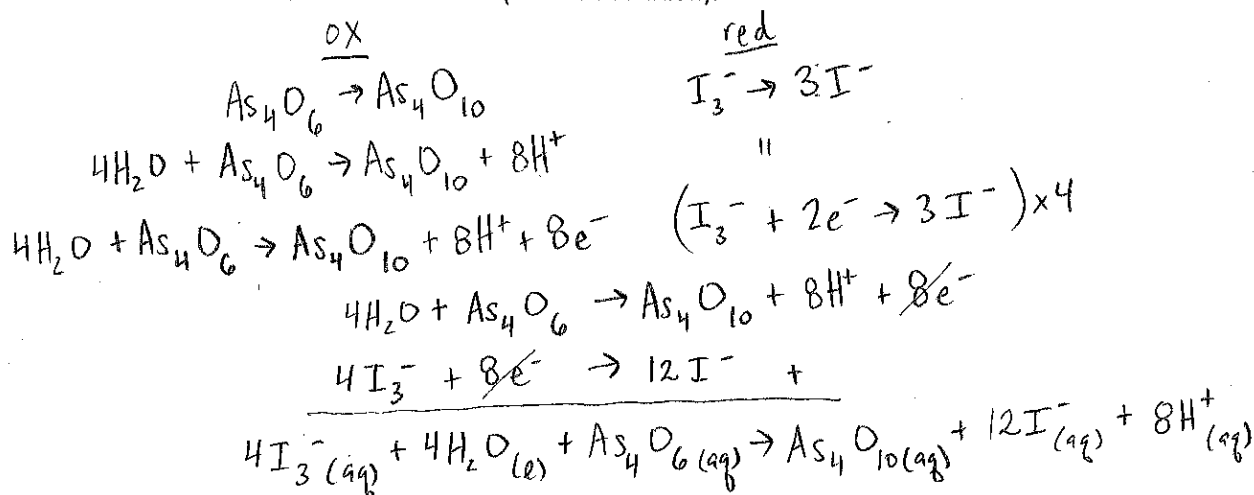
$$37.30 - 5.65 = 31.65 \text{ mL KMnO}_4 \text{ added}$$

## Let's Practice!

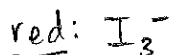
1. A solution of  $I_3^-(aq)$  can be standardized by using it to titrate  $As_4O_6(aq)$  under acidic conditions. The titration of 0.1021 g of  $As_4O_6(aq)$  dissolved in 30.00 mL of water requires 36.55 mL of  $I_3^-(aq)$  solution to reach equivalence point. The unbalanced equation is:



- a. Balance the reaction above (in acidic solution).



- b. Identify the species oxidized and reduced in this reaction.



- c. Calculate the moles of  $As_4O_6(aq)$  present in the initial sample.

$$0.1021 \text{ g } As_4O_6 \times \frac{1 \text{ mol } As_4O_6}{395.68 \text{ g } As_4O_6} = 2.580 \times 10^{-4} \text{ mol } As_4O_6$$

- d. Calculate the initial  $[As_4O_6]$ .

$$[As_4O_6] = \frac{2.580 \times 10^{-4} \text{ mol}}{0.03000 \text{ L}} = 8.600 \times 10^{-2} \text{ M } As_4O_6$$

- e. How many moles of  $I_3^-(aq)$  were added to reach equivalence point?

$$2.580 \times 10^{-4} \text{ mol } As_4O_6 \times \frac{4 \text{ mol } I_3^-}{1 \text{ mol } As_4O_6} = 1.032 \times 10^{-3} \text{ mol } I_3^-$$

- f. Calculate  $[I_3^-]$ .

$$[I_3^-] = \frac{1.032 \times 10^{-3} \text{ mol}}{0.03655 \text{ L}} = 2.824 \times 10^{-2} \text{ M } I_3^-$$

### Potential Titration Lab Errors:

#### 1. Over-titration

- a. **Cause:** going past the equivalence point by adding too much titrant
- b. **Effect:** calculated moles of titrant  $\uparrow$   $\rightarrow$  calculated moles of analyte  $\uparrow$   $\rightarrow$  calculated [analyte] is  $>$  than actual [analyte]

#### 2. Under-titration

- a. **Cause:** not reaching the equivalence point by adding too little titrant
- b. **Effect:** calculated moles of titrant  $\downarrow$   $\rightarrow$  calculated moles of analyte  $\downarrow$   $\rightarrow$  calculated [analyte] is  $<$  than actual [analyte]

#### 3. Water added to titrant (buret)

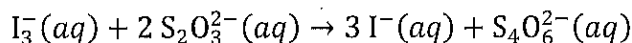
- a. **Cause:** Buret still wet from rinsing when it is filled with titrant
- b. **Effect:** Actual concentration of analyte is  $\downarrow$  than it is marked  $\rightarrow$   $\uparrow$  volume added than you should need  $\rightarrow$  calculated moles of analyte are  $\uparrow$   $\rightarrow$  calculated [analyte] is  $\uparrow$

#### 4. Water added to analyte (flask or beaker)

- a. **Cause:** Flask or beaker still wet from rinsing when it analyte (unknown) is added  $\downarrow$  solid
- b. **Effect:** moles of analyte don't change  $\rightarrow$  NO effect on [analyte]

### More practice!

2. The amount of  $I_3^-(aq)$  in a solution can be determined by titration with a solution containing a known concentration of thiosulfate,  $S_2O_3^{2-}(aq)$ . The determination is based on the balanced equation:



- a. Given that it requires 36.40 mL of 0.3300 M  $Na_2S_2O_3(aq)$  to titrate the  $I_3^-(aq)$  in a 15.00 mL sample, calculate the molarity of  $I_3^-(aq)$  in the solution.

$$0.3300 \text{ M} \times 0.03640 \text{ L} = 0.01201 \text{ mol } Na_2S_2O_3 \times \frac{1 \text{ mol } S_2O_3^{2-}}{1 \text{ mol } Na_2S_2O_3} \times \frac{1 \text{ mol } I_3^-}{2 \text{ mol } S_2O_3^{2-}}$$

$$= 0.006006 \text{ mol } I_3^- / 0.01500 \text{ L} = \boxed{0.4004 \text{ M } I_3^-}$$

- b. After performing the titration, a student determines that the molarity of  $I_3^-(aq)$  that they calculated was larger than the actual molarity of  $I_3^-(aq)$ . Explain the most likely source of their error.

*Over-titration!* they most likely added too much titrant, going past the equivalence point, thus resulting in a calculated  $[I_3^-]$  that is higher than the actual  $[I_3^-]$ .