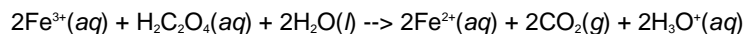


Stoichiometric Calculations

A balanced reaction, which gives the stoichiometric relationship between the moles of reactants and the moles of products, provides the basis for many analytical calculations. Consider, for example, an analysis for oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, in which Fe^{3+} oxidizes oxalic acid to CO_2 .



The balanced reaction indicates that one mole of oxalic acid reacts with two moles of Fe^{3+} . As shown in Example 2.6, we can use this balanced reaction to determine the amount of oxalic acid in a sample of rhubarb.

Example 2.6

The amount of oxalic acid in a sample of rhubarb was determined by reacting with Fe^{3+} . After extracting a 10.62 g of rhubarb with a solvent, oxidation of the oxalic acid required 36.44 mL of 0.0130 M Fe^{3+} . What is the weight percent of oxalic acid in the sample of rhubarb?

Solution

We begin by calculating the moles of Fe^{3+} used in the reaction

$$(0.0130 \text{ mol Fe}^{3+} / \text{L}) \times 0.03644 \text{ L} = 4.737 \times 10^{-4} \text{ mol Fe}^{3+}$$

The moles of oxalic acid reacting with the Fe^{3+} , therefore, is

$$4.737 \times 10^{-4} \text{ mol Fe}^{3+} \times (1 \text{ mol H}_2\text{C}_2\text{O}_4 / 2 \text{ mol Fe}^{3+}) = 2.368 \times 10^{-4} \text{ mol H}_2\text{C}_2\text{O}_4$$

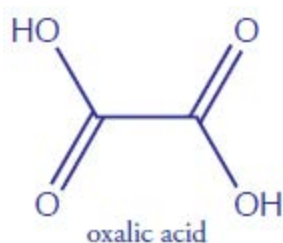
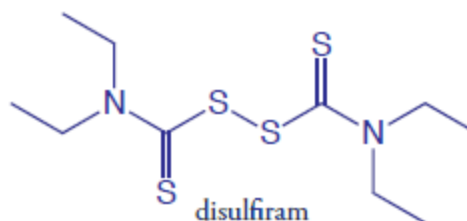
Converting the moles of oxalic acid to grams of oxalic acid

$$2.368 \times 10^{-4} \text{ mol H}_2\text{C}_2\text{O}_4 \times (90.03 \text{ g H}_2\text{C}_2\text{O}_4 / \text{mol H}_2\text{C}_2\text{O}_4) = 2.132 \times 10^{-2} \text{ g H}_2\text{C}_2\text{O}_4$$

and calculating the weight percent gives the concentration of oxalic acid in the sample of rhubarb as

$$(2.132 \times 10^{-2} \text{ g H}_2\text{C}_2\text{O}_4 / 10.62 \text{ g rhubarb}) \times 100 = 0.201\% \text{ w/w H}_2\text{C}_2\text{O}_4$$

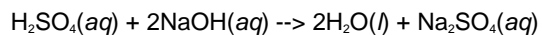
Note that we retain an extra significant figure throughout the calculation, rounding to the correct number of significant figures at the end. We will follow this convention in any problem involving more than one step. If we forget that we are retaining an extra significant figure, we might report the final answer with one too many significant figures. In this chapter we will mark the extra digit in red for emphasis. Be sure that you pick a system for keeping track of significant figures.



Oxalic acid, in sufficient amounts, is toxic. At lower physiological concentrations it leads to the formation of kidney stones. The leaves of the rhubarb plant contain relatively high concentrations of oxalic acid. The stalk, which many individuals enjoy eating, contains much smaller concentrations of oxalic acid.

The analyte in Example 2.6, oxalic acid, is in a chemically useful form because there is a reagent, Fe^{3+} , that reacts with it quantitatively. In many analytical methods, we must convert the analyte into a more accessible form before we can complete the analysis. For example, one method for the quantitative analysis of disulfiram, $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4$ —the active ingredient in the drug Anatbuse—requires that we convert the sulfur to H_2SO_4 by first oxidizing it to SO_2 by combustion, and then oxidizing the SO_2 to H_2SO_4 by bubbling it through a solution of H_2O_2 . When the conversion is complete, the amount of H_2SO_4 is determined by titrating with NaOH .

To convert the moles of NaOH used in the titration to the moles of disulfiram in the sample, we need to know the stoichiometry of the reactions. Writing a balanced reaction for H_2SO_4 and NaOH is straightforward



but the balanced reactions for the oxidations of $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4$ to SO_2 , and of SO_2 to H_2SO_4 are not as immediately obvious. Although we can balance these redox reactions, it is often easier to deduce the overall stoichiometry by using a little chemical logic.

Example 2.7

An analysis for disulfiram, $C_{10}H_{20}N_2S_4$, in Antabuse is carried out by oxidizing the sulfur to H_2SO_4 and titrating the H_2SO_4 with NaOH. If a 0.4613-g sample of Antabuse is taken through this procedure, requiring 34.85 mL of 0.02500 M NaOH to titrate the H_2SO_4 , what is the % w/w disulfiram in the sample?

Solution

Calculating the moles of H_2SO_4 is easy—first, we calculate the moles of NaOH used in the titration

$$(0.02500 \text{ M}) \times (0.03485 \text{ L}) = 8.7125 \times 10^{-4} \text{ mol NaOH}$$

and then we use the balanced reaction to calculate the corresponding moles of H_2SO_4 .

$$8.7125 \times 10^{-4} \text{ mol NaOH} \times (1 \text{ mol } H_2SO_4 / 2 \text{ mol NaOH}) = 4.3562 \times 10^{-4} \text{ mol } H_2SO_4$$

We do not need balanced reactions to convert the moles of H_2SO_4 to the corresponding moles of $C_{10}H_{20}N_2S_4$. Instead, we take advantage

of a conservation of mass—all the sulfur in $C_{10}H_{20}N_2S_4$ must end up in the H_2SO_4 (Here is where we use a little chemical logic! A conservation of mass is the essence of stoichiometry.); thus

$$4.3562 \times 10^{-4} \text{ mol } H_2SO_4 \times (1 \text{ mol S} / \text{mol } H_2SO_4) \times (1 \text{ mol } C_{10}H_{20}N_2S_4 / 4 \text{ mol S}) = 1.0890 \times 10^{-4} \text{ mol } C_{10}H_{20}N_2S_4$$

or

$$1.0890 \times 10^{-4} \text{ mol } C_{10}H_{20}N_2S_4 \times (296.54 \text{ g } C_{10}H_{20}N_2S_4 / \text{mol } C_{10}H_{20}N_2S_4) = 0.032293 \text{ g } C_{10}H_{20}N_2S_4$$

$$(0.032293 \text{ g } C_{10}H_{20}N_2S_4 / 0.4613 \text{ g sample}) \times 100 = 7.000\% \text{ w/w } C_{10}H_{20}N_2S_4$$

Source: http://chemwiki.ucdavis.edu/Analytical_Chemistry/Analytical_Chemistry_2.0/02_Basic_Tools_of_Analytical_Chemistry/2C_Stoichiometric_Calculations