

- 7-2. The equivalence point occurs when the exact stoichiometric quantities of reagents have been mixed. The end point, which comes near the equivalence point, is marked by a sudden change in a physical property brought about by the disappearance of a reactant or appearance of a product.
- 7-3. In a blank titration, the quantity of titrant required to reach the end point in the absence of analyte is measured. By subtracting this quantity from the amount of titrant needed in the presence of analyte, we reduce the systematic error.
- 7-4. In a direct titration, titrant reacts directly with analyte. In a back titration, a known excess of reagent that reacts with analyte is used. The excess is then measured with a second titrant.
- 7-5. Primary standards are purer than reagent grade chemicals. The assay of a primary standard must be very close to the nominal value (such as 99.95–100.05%), whereas the assay on a reagent chemical might be only 99%. Primary standards must have very long shelf lives.
- 7-7. 40.0 mL of 0.040 0 M  $\text{Hg}_2(\text{NO}_3)_2$  = 1.60 mmol of  $\text{Hg}_2^{2+}$ , which will require 3.20 mmol of KI. This is contained in volume =  $\frac{3.20 \text{ mmol}}{0.100 \text{ mmol/mL}} = 32.0 \text{ mL}$
- 7-8. 108.0 mL of 0.165 0 M oxalic acid = 17.82 mmol, which requires
- $$\left( \frac{2 \text{ mol MnO}_4^-}{5 \text{ mol H}_2\text{C}_2\text{O}_4} \right) (17.82 \text{ mol H}_2\text{C}_2\text{O}_4) = 7.128 \text{ mmol of MnO}_4^-.$$
- 7.128 mmol / (0.165 0 mmol/mL) = 43.20 mL of  $\text{KMnO}_4$ .
- An easy way to see this is to note that the reagents are both 0.165 0 M. Therefore, Volume of  $\text{MnO}_4^- = \frac{2}{5}$  (volume of oxalic acid).
- For the second part of the question,
- volume of oxalic acid =  $\frac{5}{2}$  (volume of  $\text{MnO}_4^-$ ) = 270.0 mL.
- 7-9. 1.69 mg of  $\text{NH}_3$  = 0.099 2 mmol of  $\text{NH}_3$ . This will react with  $\frac{3}{2}(0.099 2) = 0.149$  mmol of  $\text{OBr}^-$ . The molarity of  $\text{OBr}^-$  is 0.149 mmol/1.00 mL = 0.149 M

**7-11.** HCl added to powder = (10.00 mL)(1.396 M) = 13.96 mmol  
 NaOH required = (39.96 mL)(0.1004 M) = 4.012 mmol  
 HCl consumed by carbonate = 13.96 – 4.012 = 9.948 mmol  
 $\text{mol CaCO}_3 = \frac{1}{2} \text{mol HCl consumed} = 4.974 \text{ mmol} = 0.4978 \text{ g CaCO}_3$   
 $\text{wt\% CaCO}_3 = \frac{0.4978 \text{ g CaCO}_3}{0.5413 \text{ g limestone}} \times 100 = 92.0 \text{ wt\%}$

**7-16.** 30.10 mL of Ni<sup>2+</sup> reacted with 39.35 mL of 0.01307 M EDTA.  
 Therefore, the Ni<sup>2+</sup> molarity is

$$[\text{Ni}^{2+}] = \frac{(39.35 \text{ mL})(0.01307 \text{ mol/L})}{30.10 \text{ mL}} = 0.01709 \text{ M.}$$

25.00 mL of Ni<sup>2+</sup> contains 0.4272 mmol of Ni<sup>2+</sup>. 10.15 mL of EDTA = 0.1327 mmol of EDTA. The amount of Ni<sup>2+</sup> which must have reacted with CN<sup>-</sup> was 0.4272 – 0.1327 = 0.2945 mmol. The cyanide which reacted with Ni<sup>2+</sup> must have been (4)(0.2945) = 1.178 mmol. [CN<sup>-</sup>] = 1.178 mmol/12.73 mL = 0.09254 M.