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Titrations

Chemists have many methods for determining the quantity of a substance present in a solution or other mixture. One common method is titration, in which a solution of known concentration reacts with a sample containing the substance of unknown quantity. There are two main requirements for making titration possible. Both substances must react quickly and completely with each other, and there must be a way of knowing when the substances have reacted in precise stoichiometric quantities.

The most common titrations are acid-base titrations. These reactions are easily monitored by keeping track of pH changes with a pH meter or by choosing an indicator that changes color when the acid and base have reacted in stoichiometric quantities. This point is referred to as the *equivalence point.* Look at the following equation for the neutralization of KOH with HCl.

$$KOH(aq) + HCl(aq) \rightarrow KCl(aq) + H_2O(l)$$

Suppose you have a solution that contains 1.000 mol of KOH. All of the KOH will have reacted when 1.000 mol of HCl has been added. This is the equivalence point of this reaction.

Titration calculations rely on the relationship between volume, concentration, and amount.

$$\textit{volume of solution} \times \textit{molarity of solution} = \textit{amount of solute in moles}$$

If a titration were carried out between KOH and HCl, according the reaction above, the amount in moles of KOH and HCl would be equal at the equivalence point. The following relationship applies to this system:

$$\textit{molarity}_{KOH} \times \textit{volume}_{KOH} = \textit{amount of KOH in moles}$$
$$\textit{amount of KOH in moles} = \textit{amount of HCl in moles}$$
$$\textit{amount of HCl in moles} = \textit{molarity}_{HCl} \times \textit{volume}_{HCl}$$

Therefore:

$$\textit{molarity}_{KOH} \times \textit{volume}_{KOH} = \textit{molarity}_{HCl} \times \textit{volume}_{HCl}$$

The following plan for solving titration problems may be applied to any acid-base titration, regardless of whether the equivalence point occurs at equivalent volumes.

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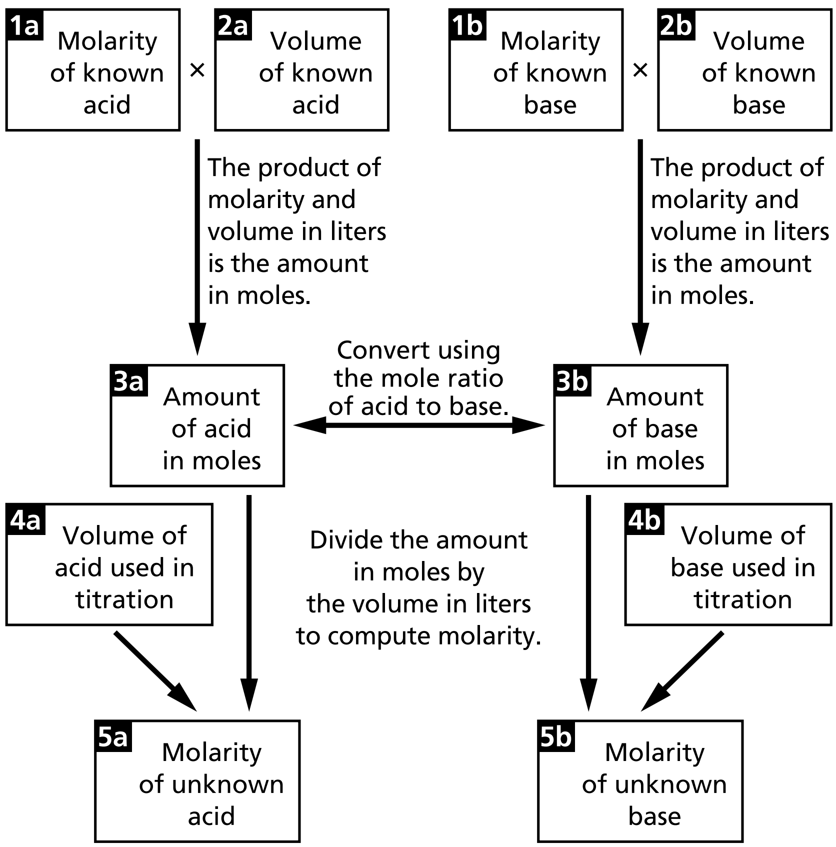
General Plan for Solving Titration Problems



SAMPLE PROBLEM 1

A titration of a 25.00 mL sample of a hydrochloric acid solution of unknown molarity reaches the equivalence point when 38.28 mL of 0.4370 M NaOH solution has been added. What is the molarity of the HCl solution?

$$\mathbf{HCl}(aq) + \mathbf{NaOH}(aq) \rightarrow \mathbf{NaCl}(aq) + \mathbf{H_2O}(l)$$

SOLUTION

1. *ANALYZE*

- *What is given in the problem?* — the volume of the HCl solution titrated, and the molarity and volume of NaOH solution used in the titration
- *What are you asked to find?* — the molarity of the HCl solution

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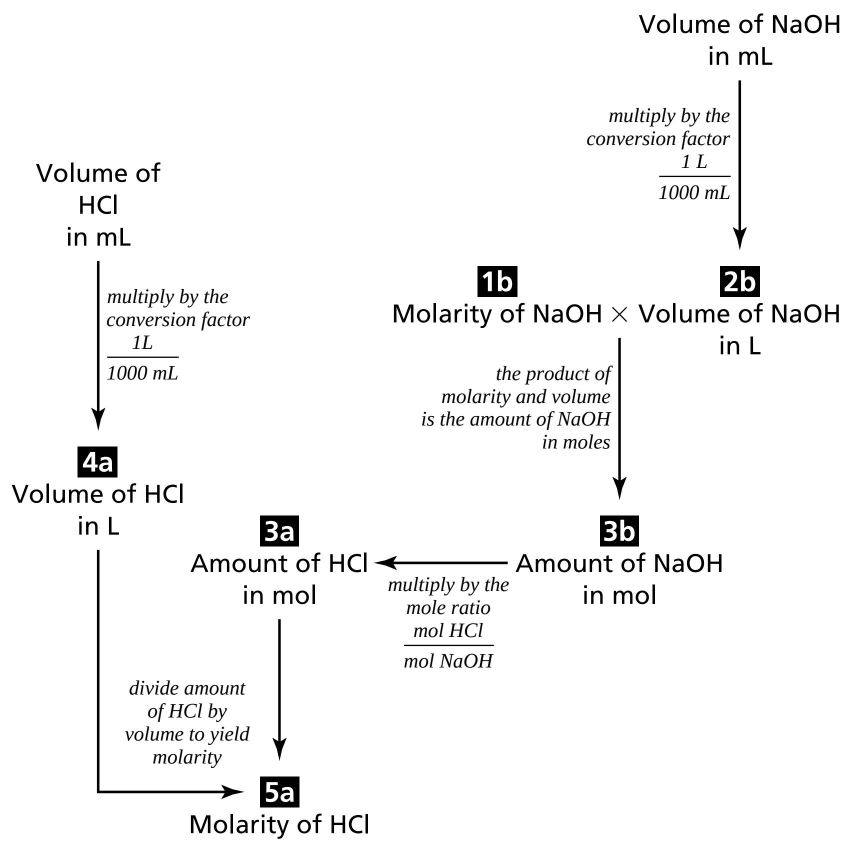
Items	**Data**
Volume of acid solution	25.00 mL
Molarity of acid solution	**?** M
Mole ratio of base to acid in titration reaction	1 mol base:1 mol acid
Volume of base solution	38.28 mL
Molarity of base solution	0.4370 M

2. *PLAN*

- *What steps are needed to calculate the molarity of the HCl solution?*

Use the volume and molarity of the NaOH to calculate the number of moles of NaOH that reacted. Use the mole ratio between base and acid to determine the moles of HCl that reacted. Use the volume of the acid to calculate molarity.



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$$\overset{given}{\text{mL NaOH}} \times \frac{1\ \text{L}}{1000\ \text{mL}} = \text{L NaOH}$$

$$\overset{given}{\text{mL HCl}} \times \frac{1\ \text{L}}{1000\ \text{mL}} = \text{L HCl}$$

$$\overset{\text{calculated above}}{\text{L NaOH}} \times \overset{given}{\frac{\text{mol NaOH}}{\text{L NaOH}}} \times \overset{\text{given in balanced chemical equation}}{\frac{1\ \text{mol HCl}}{1\ \text{mol NaOH}}} \times \overset{\text{calculated above}}{\frac{1}{\text{L HCl}}} = \text{M HCl}$$

3. *COMPUTE*

$$38.28\ \cancel{\text{mL}}\ \text{NaOH} \times \frac{1\ \text{L}}{1000\ \cancel{\text{mL}}} = 0.03828\ \text{L NaOH}$$

$$25.00\ \cancel{\text{mL}}\ \text{HCl} \times \frac{1\ \text{L}}{1000\ \cancel{\text{mL}}} = 0.02500\ \text{L HCl}$$

$$0.03828\ \cancel{\text{L NaOH}} \times \frac{0.4370\ \cancel{\text{mol NaOH}}}{\cancel{\text{L NaOH}}} \times \frac{1\ \text{mol HCl}}{1\ \cancel{\text{mol NaOH}}} \times \frac{1}{0.02500\ \text{L HCl}} = 0.6691\ \text{M HCl}$$

4. *EVALUATE*

- *Are the units correct?* — Yes; molarity, or mol/L, was required.
- *Is the number of significant figures correct?* — Yes; the number of significant figures is correct because all data were given to four significant figures.
- *Is the answer reasonable?* — Yes; a larger volume of base was required than the volume of acid used. Therefore, the HCl must be more concentrated than the NaOH.

PRACTICE

In each of the following problems, the acids and bases react in a mole ratio of 1 mol base : 1 mol acid.

1. A student titrates a 20.00 mL sample of a solution of HBr with unknown molarity. The titration requires 20.05 mL of a 0.1819 M solution of NaOH. What is the molarity of the HBr solution? *ans:* 0.1824 M HBr

2. Vinegar can be assayed to determine its acetic acid content. Determine the molarity of acetic acid in a 15.00 mL sample of vinegar that requires 22.70 mL of a 0.550 M solution of NaOH to reach the equivalence point. *ans:* 0.832 M

SAMPLE PROBLEM 2

A 50.00 mL sample of a sodium hydroxide solution is titrated with a 1.605 M solution of sulfuric acid. The titration requires 24.09 mL of the acid solution to reach the equivalence point. What is the molarity of the base solution?

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$$

SOLUTION

1. *ANALYZE*

- *What is given in the problem?* the balanced chemical equation for the acid-base reaction, the volume of the base solution, and the molarity and volume of the acid used in the titration
- *What are you asked to find?* the molarity of the sodium hydroxide solution

Items	Data
Volume of acid solution	24.09 mL
Molarity of acid solution	1.605 M
Mole ratio of base to acid in titration reaction	2 mol base: 1 mol acid
Volume of base solution	50.00 mL
Molarity of base solution	**?** M

2. *PLAN*

- *What steps are needed to calculate the molarity of the NaOH solution?* Use the volume and molarity of the acid to calculate the number of moles of acid that reacted. Use the mole ratio between base and acid to determine the moles of base that reacted. Use the volume of the base to calculate molarity.

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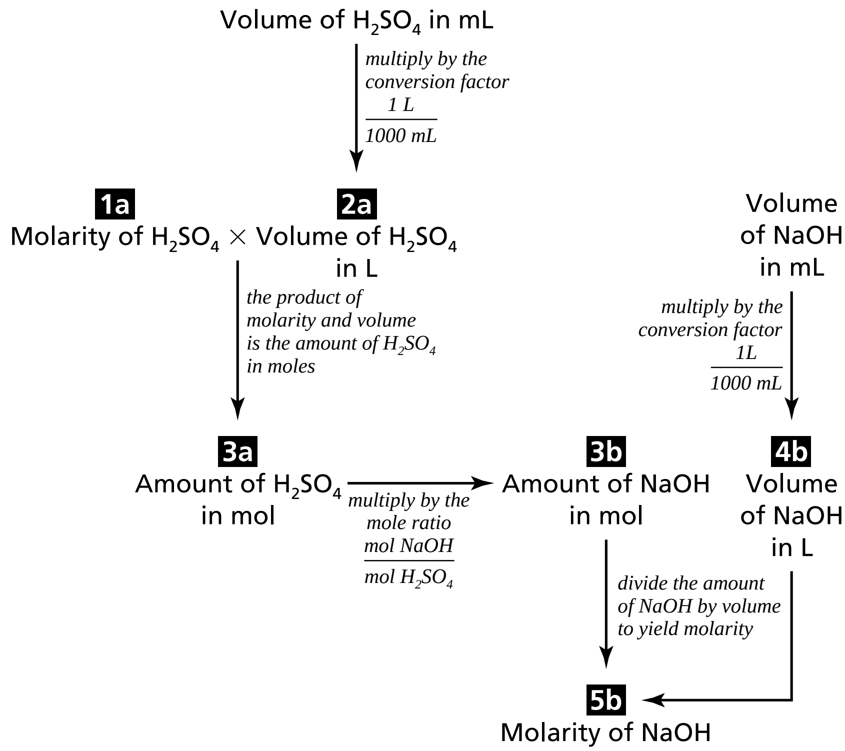

$$\overset{given}{\text{mL NaOH}} \times \frac{1\text{ L}}{1000\text{ mL}} = \text{L NaOH}$$

$$\overset{given}{\text{mL } H_2SO_4} \times \frac{1\text{ L}}{1000\text{ mL}} = \text{L } H_2SO_4$$

$$\overset{\text{calculated above}}{\text{L } H_2SO_4} \times \overset{given}{\frac{\text{mol } H_2SO_4}{\text{L } H_2SO_4}} \times \overset{\text{given in balanced chemical equation}}{\frac{2\text{ mol NaOH}}{1\text{ mol } H_2SO_4}} \times \overset{\text{calculated above}}{\frac{1}{\text{L NaOH}}} = \text{M NaOH}$$

3. *COMPUTE*

$$50.00\ \cancel{\text{mL}}\text{ NaOH} \times \frac{1\text{ L}}{1000\ \cancel{\text{mL}}} = 0.05000\text{ L NaOH}$$

$$24.09\ \cancel{\text{mL}}\ H_2SO_4 \times \frac{1\text{ L}}{1000\ \cancel{\text{mL}}} = 0.02409\text{ L } H_2SO_4$$

$$0.02409\ \cancel{\text{L } H_2SO_4} \times \frac{1.605\ \cancel{\text{mol } H_2SO_4}}{\cancel{\text{L } H_2SO_4}} \times \frac{2\text{ mol NaOH}}{1\ \cancel{\text{mol } H_2SO_4}}$$

$$\times \frac{1}{0.05000\text{ L NaOH}} = 1.547\text{ M NaOH}$$

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4. *EVALUATE*

- *Are the units correct?* Yes; molarity was required.
- *Is the number of significant figures correct?* Yes; the number of significant figures is correct because all data were given to four significant figures.
- *Is the answer reasonable?* Yes; the volume of acid required was approximately half the volume of base used. Because of the 1:2 mole ratio, the acid must be about the same as the concentration of the base, which agrees with the result obtained.

PRACTICE

1. A 20.00 mL sample of a solution of $Sr(OH)_2$ is titrated to the equivalence point with 43.03 mL of 0.1159 M HCl. What is the molarity of the $Sr(OH)_2$ solution? *ans:* 0.1247 M $Sr(OH)_2$

2. A 35.00 mL sample of ammonia solution is titrated to the equivalence point with 54.95 mL of a 0.400 M sulfuric acid solution. What is the molarity of the ammonia solution? *ans:* 1.26 M NH_3

SAMPLE PROBLEM 3

A supply of NaOH is known to contain the contaminants NaCl and $MgCl_2$. A 4.955 g sample of this material is dissolved and diluted to 500.00 mL with water. A 20.00 mL sample of this solution is titrated with 22.26 mL of a 0.1989 M solution of HCl. What percentage of the original sample is NaOH? Assume that none of the contaminants react with HCl.

SOLUTION

1. *ANALYZE*

- *What is given in the problem?* the mass of the original solute sample, the volume of the solution of the sample, the volume of the sample taken for titration, the molarity of the acid solution, and the volume of the acid solution used in the titration

- *What are you asked to find?* the percentage by mass of NaOH in the original sample

Items	Data
Volume of acid solution	22.26 mL
Molarity of acid solution	0.1989 M
Mole ratio of base to acid in titration reaction	?
Volume of base solution titrated	20.00 mL
Moles of base in solution titrated	? mol NaOH
Volume of original sample solution	500.00 mL
Moles of base in original sample	? mol NaOH
Mass of original sample	4.955 g impure NaOH
Mass of base in original sample	? g NaOH
Percentage of NaOH in original sample	?% NaOH

2. *PLAN*

- *What steps are needed to calculate the concentration of NaOH in the sample?* Determine the balanced chemical equation for the titration reaction. Use the volume and molarity of the HCl to calculate the number of moles of HCl that reacted. Use the mole ratio between base and acid to determine the amount of NaOH that reacted. Divide by the volume titrated to obtain the concentration of NaOH.
- *What steps are needed to calculate the percentage of NaOH in the sample?* Convert the concentration of NaOH to the amount of NaOH in the original sample by multiplying the concentration by the total volume. Convert amount of NaOH to mass NaOH by using the molar mass of NaOH. Use the mass of NaOH and the mass of the sample to calculate the percentage of NaOH.

You must first determine the equation for titration reaction.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

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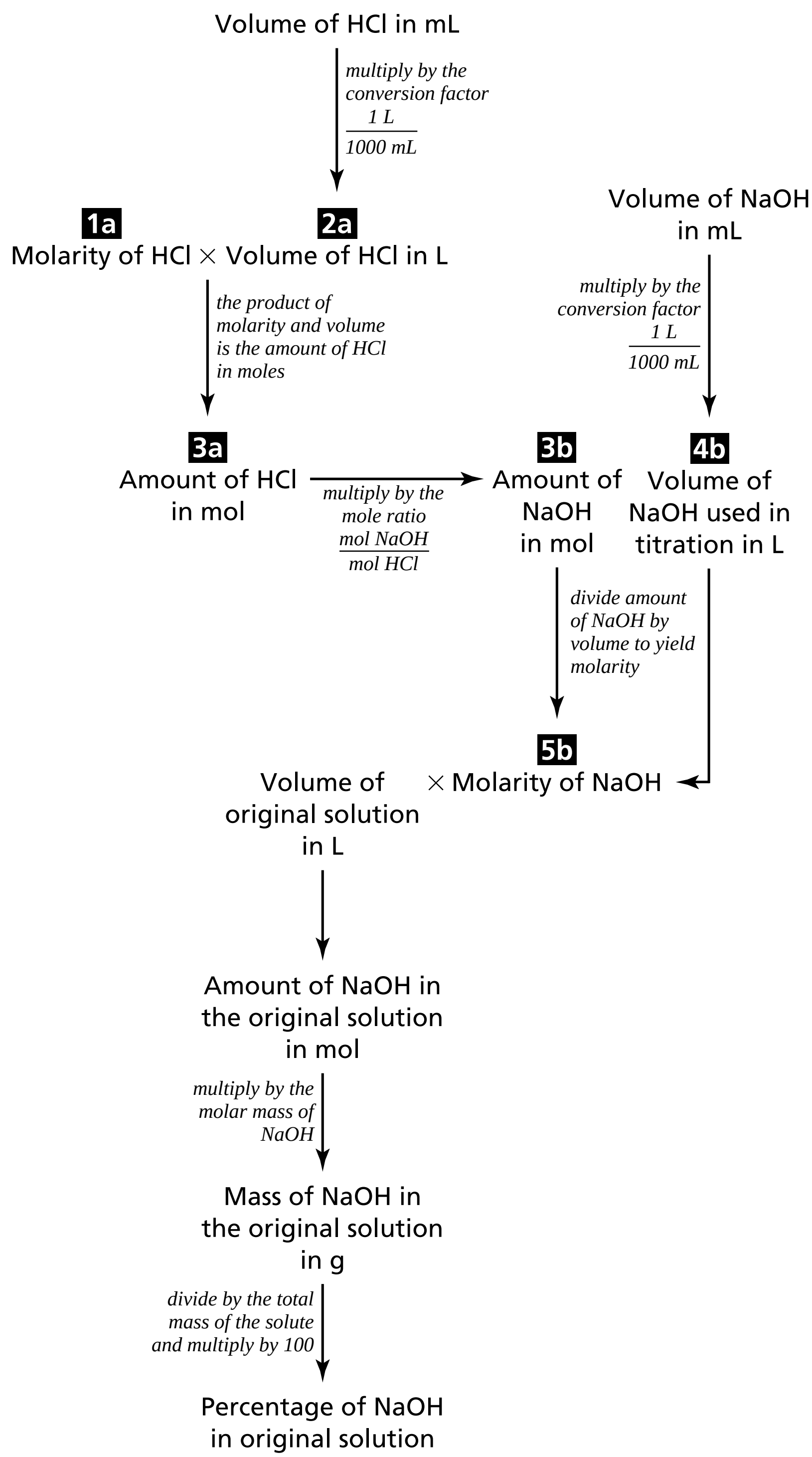

$$\overset{\textit{given}}{\text{mL NaOH}_{titrated}} \times \frac{1\text{ L}}{1000\text{ mL}} = \text{L NaOH}_{titrated}$$

$$\overset{\textit{given}}{\text{mL HCl}} \times \frac{1\text{ L}}{1000\text{ mL}} = \text{L HCl}$$

$$\overset{\substack{\textit{calculated}\\ \textit{above}}}{\text{L HCl}} \times \overset{\textit{given}}{\frac{\text{mol HCl}}{\text{L HCl}}} \times \overset{\substack{\textit{given in balanced}\\ \textit{chemical equation}}}{\frac{1\text{ mol NaOH}}{1\text{ mol HCl}}} \times \overset{\substack{\textit{calculated}\\ \textit{above}}}{\frac{1}{\text{L NaOH}_{titrated}}} = \text{M NaOH}$$

$$\overset{\textit{given}}{\text{mL NaOH}_{original}} \times \frac{1\text{ L}}{1000\text{ mL}} = \text{L NaOH}_{original}$$

$$\overset{\textit{calculated above}}{\frac{\text{mol NaOH}}{\text{L NaOH}}} \times \overset{\textit{calculated above}}{\text{L NaOH}_{original}} \times \overset{\textit{molar mass of NaOH}}{\frac{40.00\text{ g NaOH}}{\text{mol NaOH}}} = \text{g NaOH}_{original}$$

$$\frac{\overset{\textit{calculated above}}{\text{g NaOH}_{original}}}{\underset{\textit{given}}{\text{g solute}}} \times 100 = \text{percentage of NaOH in solute}$$

3. *COMPUTE*

$$20.00\ \cancel{\text{mL}}\ \text{NaOH}_{titrated} \times \frac{1\text{ L}}{1000\ \cancel{\text{mL}}} = 0.02000\text{ L NaOH}_{titrated}$$

$$22.26\ \cancel{\text{mL}}\ \text{HCl} \times \frac{1\text{ L}}{1000\ \cancel{\text{mL}}} = 0.02226\text{ L HCl}$$

$$0.02226\ \cancel{\text{L HCl}} \times \frac{0.1989\ \cancel{\text{mol HCl}}}{\cancel{\text{L HCl}}} \times \frac{1\text{ mol NaOH}}{1\ \cancel{\text{mol HCl}}} \times \frac{1}{0.02000\text{ L NaOH}} = 0.2214\text{ M NaOH}$$

$$500.00\ \cancel{\text{mL}}\ \text{NaOH}_{original} \times \frac{1\text{ L}}{1000\ \cancel{\text{mL}}} = 0.500\ 00\text{ L NaOH}_{original}$$

$$\frac{0.2214\ \cancel{\text{mol NaOH}}}{\cancel{\text{L NaOH}}} \times 0.500\ 00\ \cancel{\text{L NaOH}} \times \frac{40.00\text{ g NaOH}}{\cancel{\text{mol NaOH}}} = 4.428\text{ g NaOH}$$

$$\frac{4.428\text{ g NaOH}}{4.955\text{ g solute}} \times 100 = 89.35\%\text{ NaOH}$$

4. *EVALUATE*

- *Are the units correct?* Yes; units canceled to give percentage of NaOH in sample.

- *Is the number of significant figures correct?* Yes; the number of significant figures is correct because all data were given to four significant figures.
- *Is the answer reasonable?* Yes; the calculation can be approximated as $(0.02 \times 0.2 \times 25 \times 40 \times 100)/5 = 400/5 = 80$, which is close to the calculated result.

PRACTICE

In the problems below, assume that impurities are not acidic or basic and that they do not react in an acid-base titration.

1. A supply of glacial acetic acid has absorbed water from the air. It must be assayed to determine the actual percentage of acetic acid. 2.000 g of the acid is diluted to 100.00 mL, and 20.00 mL is titrated with a solution of sodium hydroxide. The base solution has a concentration of 0.218 M, and 28.25 mL is used in the titration. Calculate the percentage of acetic acid in the original sample. Write the titration equation to get the mole ratio. *ans:* 92.5% acetic acid
2. A shipment of crude sodium carbonate must be assayed for its Na_2CO_3 content. You receive a small jar containing a sample from the shipment and weigh out 9.709 g into a flask, where it is dissolved in water and diluted to 1.0000 L with distilled water. A 10.00 mL sample is taken from the flask and titrated to the equivalence point with 16.90 mL of a 0.1022 M HCl solution. Determine the percentage of Na_2CO_3 in the sample. Write the titration equation to get the mole ratio. *ans:* 94.28% Na_2CO_3

ADDITIONAL PROBLEMS

1. A 50.00 mL sample of a potassium hydroxide is titrated with a 0.8186 M HCl solution. The titration requires 27.87 mL of the HCl solution to reach the equivalence point. What is the molarity of the KOH solution?

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2. A 15.00 mL sample of acetic acid is titrated with 34.13 mL of 0.9940 M NaOH. Determine the molarity of the acetic acid.
3. A 12.00 mL sample of an ammonia solution is titrated with 1.499 M HNO_3 solution. A total of 19.48 mL of acid is required to reach the equivalence point. What is the molarity of the ammonia solution?
4. A certain acid and base react in a 1 : 1 ratio.
   - **a.** If the acid and base solutions are of equal concentration, what volume of acid will titrate a 20.00 mL sample of the base?
   - **b.** If the acid is twice as concentrated as the base, what volume of acid will be required to titrate 20.00 mL of the base?
   - **c.** How much acid will be required if the base is four times as concentrated as the acid, and 20.00 mL of base is used?
5. A 10.00 mL sample of a solution of hydrofluoric acid, HF, is diluted to 500.00 mL. A 20.00 mL sample of the diluted solution requires 13.51 mL of a 0.1500 M NaOH solution to be titrated to the equivalence point. What is the molarity of the original HF solution?
6. A solution of oxalic acid, a diprotic acid, is used to titrate a 16.22 mL sample of a 0.5030 M KOH solution. If the titration requires 18.41 mL of the oxalic acid solution, what is its molarity?
7. A H_2SO_4 solution of unknown molarity is titrated with a 1.209 M NaOH solution. The titration requires 42.27 mL of the NaOH solution to reach the equivalent point with 25.00 mL of the H_2SO_4 solution. What is the molarity of the acid solution?
8. Potassium hydrogen phthalate, $KHC_8H_4O_4$, is a solid acidic substance that reacts in a 1 : 1 mole ratio with bases that have one hydroxide ion. Suppose that 0.7025 g of potassium hydrogen phthalate is titrated to the equivalence point by 20.18 mL of a KOH solution. What is the molarity of the KOH solution?
9. A solution of citric acid, a triprotic acid, is titrated with a sodium hydroxide solution. A 20.00 mL sample of the citric acid solution requires 17.03 mL of a 2.025 M solution of NaOH to reach the equivalence point. What is the molarity of the acid solution?
10. A flask contains 41.04 mL of a solution of potassium hydroxide. The solution is titrated and reaches an equivalence point when 21.65 mL of a 0.6515 M solution of HNO_3 is added. Calculate the molarity of the base solution.
11. A bottle is labeled 2.00 M H_2SO_4. You decide to titrate a 20.00 mL sample with a 1.85 M NaOH solution. What volume of NaOH solution would you expect to use if the label is correct?
12. What volume of a 0.5200 M solution of H_2SO_4 would be needed to titrate 100.00 mL of a 0.1225 M solution of $Sr(OH)_2$?

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13. A sample of a crude grade of KOH is sent to the lab to be tested for KOH content. A 4.005 g sample is dissolved and diluted to 200.00 mL with water. A 25.00 mL sample of the solution is titrated with a 0.4388 M HCl solution and requires 19.93 mL to reach the equivalence point. How many moles of KOH were in the 4.005 g sample? What mass of KOH is this? What is the percent KOH in the crude material?

14. What mass of magnesium hydroxide would be required for the magnesium hydroxide to react to the equivalence point with 558 mL of 3.18 M hydrochloric acid?

15. An ammonia solution of unknown concentration is titrated with a solution of hydrochloric acid. The HCl solution is 1.25 M, and 5.19 mL are required to titrate 12.61 mL of the ammonia solution. What is the molarity of the ammonia solution?

16. What volume of 2.811 M oxalic acid solution is needed to react to the equivalence point with a 5.090 g sample of material that is 92.10% NaOH? Oxalic acid is a diprotic acid.

17. Standard solutions of accurately known concentration are available in most laboratories. These solutions are used to titrate other solutions to determine their concentrations. Once the concentration of the other solutions are accurately known, they may be used to titrate solutions of unknowns.

The molarity of a solution of HCl is determined by titrating the solution with an accurately known solution of $Ba(OH)_2$, which has a molar concentration of 0.1529 M. A volume of 43.09 mL of the $Ba(OH)_2$ solution titrates 26.06 mL of the acid solution. The acid solution is in turn used to titrate 15.00 mL of a solution of rubidium hydroxide. The titration requires 27.05 mL of the acid.

a. What is the molarity of the HCl solution?

b. What is the molarity of the RbOH solution?

18. A truck containing 2800 kg of a 6.0 M hydrochloric acid has been in an accident and is in danger of spilling its load. What mass of $Ca(OH)_2$ should be sent to the scene in order to neutralize all of the acid in case the tank bursts? The density of the 6.0 M HCl solution is 1.10 g/mL.

19. A 1.00 mL sample of a fairly concentrated nitric acid solution is diluted to 200.00 mL. A 10.00 mL sample of the diluted solution requires 23.94 mL of a 0.0177 M solution of $Ba(OH)_2$ to be titrated to the equivalence point. Determine the molarity of the original nitric acid solution.

20. What volume of 4.494 M H_2SO_4 solution would be required to react to the equivalence point with 7.2280 g of LiOH(*s*)?