

**Example 2-6: Determining total alkalinity** A 200-mL sample of water has an initial pH of 10. Thirty milliliters of 0.02 N H<sub>2</sub>SO<sub>4</sub> is required to titrate the sample to pH 4.5. What is the total alkalinity of the water in milligrams per liter as CaCO<sub>3</sub>?

SOLUTION

Because each mg of 0.02 N H<sub>2</sub>SO<sub>4</sub> will neutralize 1 mg of alkalinity, there is 30 mg of alkalinity in the 200-mL sample. Therefore, the concentration of alkalinity expressed as milligrams per liter will be

$$\frac{30 \text{ mg}}{200 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} = 150 \text{ mg/L}$$

If the volume of acid needed to reach the 8.3 endpoint is known, the species of alkalinity can also be determined. Because all of the hydroxide and one-half of the carbonate have been neutralized at pH 8.3, the acid required to lower the pH from 8.3 to 4.5 must measure the other one-half of the carbonate, plus all of the original bicarbonate. If P is the amount of acid required to reach pH 8.3 and M is the total quantity of acid required to reach 4.5, the following generalizations concerning the forms of alkalinity can be made:

- if P = M, all alkalinity is OH<sup>-</sup>
- P = M/2, all alkalinity is CO<sub>3</sub><sup>2-</sup>
- P = 0 (i.e., initial pH is below 8.3), all alkalinity is HCO<sub>3</sub><sup>-</sup>
- P < M/2, predominant species are CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup>
- P > M/2, predominant species are OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup>

In observing the pH dependency of the species in Fig. 2-3, it is noted that the quantity of OH<sup>-</sup> becomes significant at pH less than about 9.0. Without introducing significant error, it can be assumed that the OH<sup>-</sup> of samples with pH less than 9.0 is insignificant. The CO<sub>3</sub><sup>2-</sup> would then be measured by 2P and the HCO<sub>3</sub><sup>-</sup> would be measured by the remainder (M - 2P). One method of calculating the quantities of each species is illustrated in the following example.

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