

**Table 7.3**  
Commonly Used Indicator Solutions

common name	pH visual transition interval	color	
		acidic	basic
cresol red	0.2 - 1.8	red	yellow
thymol blue	1.2 - 2.8	red	yellow
methyl yellow	2.4 - 4.0	red	yellow
bromophenol blue	3.0 - 4.6	yellow	blue
methyl orange	3.2 - 4.4	red	yellow-orange
methyl orange + xylene cyanole FF, 40 : 56	(3.8 - 4.1) <sup>a</sup>	violet	green
bromocresol green	3.9 - 5.4	yellow	blue
methyl red	4.2 - 6.2	pink	yellow
methyl red + methylene blue, 1 : 1	(~ 5.3) <sup>a</sup>	red-violet	green
bromocresol purple	5.2 - 6.8	yellow	purple
bromothymol blue	6.0 - 7.6	yellow	blue
cresol red	7.2 - 8.8	yellow	red
phenol red	6.8 - 8.2	yellow	red
thymol blue	8.0 - 9.2	yellow	blue
phenolphthalein	(8.0 - 9.8) <sup>b</sup>	colorless	red-violet
phenolphthalein + methylene green, 1 : 2	(8.8) <sup>c</sup>	green	violet
thymolphthalein	(9.0 - 10.5) <sup>b</sup>	colorless	blue
eriochrome black T	7 - 10	blue	wine-red
alizarin yellow	10.1 - 12	yellow	red

<sup>a</sup> Screened indicator, neutral gray at stated pH.

<sup>b</sup> Based on addition of 1 or 2 drops of a 0.1% indicator solution to 10 ml of aqueous solution

<sup>c</sup> Screened indicator, pale blue at stated pH

For strongly basic samples (pH > 8.3), consecutive titration with both phenolphthalein and methyl orange is often done. The alkalinity is the sum total of the *phenolphthalein alkalinity* and the *methyl orange alkalinity*. (Note: Phenolphthalein alkalinity is not the same as carbonate alkalinity since  $\text{CO}_3^{2-}$  has been converted to  $\text{HCO}_3^-$  but not neutralized. See equation 7.17. The *carbonate alkalinity* is twice the phenolphthalein alkalinity.)

*Example 7.14*

0.02N sulfuric acid is used to titrate 110 ml of water. 3.3 ml of titrant is needed to reach the phenolphthalein point, and 13.2 ml is needed to reach the methyl orange point. What are the total and phenolphthalein alkalinities?

From equation 7.19, the phenolphthalein alkalinity is

$$(3.3)(0.02)(50,000)/(110) = 30 \text{ mg/l as CaCO}_3$$

The total alkalinity is

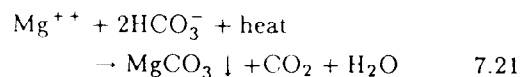
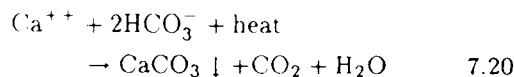
$$(13.2 + 3.3)(0.02)(50,000)/(110) = 150 \text{ mg/l as CaCO}_3$$

The alkalinity of 150 mg/l is caused by carbonates ( $2 \times 30 = 60 \text{ mg/l}$ ) and bicarbonates ( $150 - 60 = 90 \text{ mg/l}$ ).

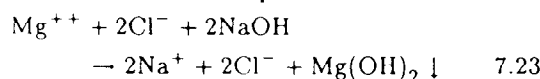
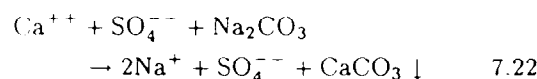
**B. HARDNESS**

Water hardness is caused by multi-valent (doubly-charged, triply-charged, etc., but not singly-charged) positive metallic ions such as calcium, magnesium, iron, and manganese. (Iron and manganese are not as common, however.) Hardness reacts with soap to reduce its cleansing effectiveness, and to form scum on the water surface and ring around the bathtub.

Water containing bicarbonate ( $\text{HCO}_3^-$ ) ions can be heated to precipitate a carbonate molecule.<sup>3</sup> This hardness is known as *temporary hardness* or *carbonate hardness*.<sup>4</sup>



Remaining hardness due to sulfates, chlorides, and nitrates is known as *permanent hardness* or *non-carbonate hardness* because it cannot be removed by heating. Permanent hardness can be calculated numerically by causing precipitation, drying, and then weighing the precipitate.



*Total hardness* is the sum of temporary and permanent hardnesses, both expressed in mg/l as  $\text{CaCO}_3$ .

Hardness can also be measured by the titration method using a titrant (complexione, versene, EDTA, or BDH)

<sup>3</sup> Hard water forms scale when heated. This scale, if it forms in pipes, eventually restricts water flow. Even in small quantities, the scale insulates boiler tubes. Therefore, water used in steam-producing equipment must be essentially hardness-free.

<sup>4</sup> The hardness is known as *carbonate hardness* even though it is caused by *bicarbonate* radicals, not carbonate radicals