Table 7.3
Commonly Used Indicator Solutions

common name	pH visual transition interval	color acidic	color 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)[a]	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)[a]	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
phenol-phthalein	(8.0 9.8)[b]	colorless	red-violet
phenol-phthalein + methylene green, 1 : 2	(8.8)[c]	green	violet
thymol-phthalein	(9.0 10.5)[b]	colorless	blue
eriochrome black T	7 10	blue	wine-red
alizarin yellow	10.1 12	yellow	red

[a] Screened indicator, neutral gray at stated pH.

[b] Based on addition of 1 or 2 drops of a 0.1% indicator solution to 10 ml of aqueous solution

[c] 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 CO_3^{--} has been converted to 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 × 30 = 60 mg/l) and bicarbonates (150 − 60 = 90 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 (HCO_3^-) ions can be heated to precipitate a carbonate molecule.[3] This hardness is known as *temporary hardness* or *carbonate hardness*.[4]

$$Ca^{++} + 2HCO_3^- + \text{heat} \rightarrow CaCO_3\downarrow + CO_2 + H_2O \qquad 7.20$$

$$Mg^{++} + 2HCO_3^- + \text{heat} \rightarrow MgCO_3\downarrow + CO_2 + H_2O \qquad 7.21$$

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.

$$Ca^{++} + SO_4^{--} + Na_2CO_3 \rightarrow 2Na^+ + SO_4^{--} + CaCO_3\downarrow \qquad 7.22$$

$$Mg^{++} + 2Cl^- + 2NaOH \rightarrow 2Na^+ + 2Cl^- + Mg(OH)_2\downarrow \qquad 7.23$$

Total hardness is the sum of temporary and permanent hardnesses, both expressed in mg/l as $CaCO_3$.

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

[3] 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.

[4] The hardness is known as *carbonate* hardness even though it is caused by *bicarbonate* radicals, not carbonate radicals.