

Alkalinity

Definition

- * Measure of of water's capacity to neutralize acids=Acid neutralizing capacity
- * Without this acid-neutralizing capacity, any acid added to a stream would cause an immediate change in the pH.



- * Alkalinity in natural water is due to:

- * Salts of weak acids

- * **Carbonate, bicarbonate**

- * Borate, silicate, phosphate

- * A few organic acids resistant to biological oxidation (humic subs.)

- * In polluted or anaerobic waters → Acetic, propionic acid, H₂S

- * Weak or strong bases

- * Ammonia

- * **Hydroxides**

Types of alkalinity in natural waters :

1. Hydroxide
 2. Carbonate
 3. Bicarbonate
- * For most practical conditions, alkalinity due to other materials in natural waters is insignificant and can be ignored

Public Health Significance

- * The alkalinity of water has little public health significance.
- * High alkaline waters are usually unpalatable

Alkalinity Measurement

- * Titration with N/50 H_2SO_4
- * Reported in terms of mg/L CaCO_3
 - * specifies that the sample has an alkalinity equal to that of a solution with a certain amount of calcium carbonate (CaCO_3) dissolved in water.
- * If sample pH > 8.3 \rightarrow titration is done in two steps
 - * 1. Titration until pH=8.3 (till phenolphthalein end point- pink to colorless-)
 - * 2. Titration until pH=4.5 (till bromcresol end point)



A simple example

$$\text{Alkalinity} \frac{\text{eq}}{\text{L}} \times \frac{1 \text{ mol CaCO}_3}{2 \text{ eq}} \times \frac{100.09 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} \times \frac{1000 \text{ mg}}{1 \text{ g}} = \text{Alkalinity (mg/L as CaCO}_3)$$

$$0.01 \text{ M } [\text{HCO}_3^-]$$

$$10 \text{ meq/L} * 50 \text{ mg/meq} = 500 \text{ mg/L}$$

$$\text{Alk}_T = \frac{\text{mL}_{\text{acid}} \times N_{\text{acid}} \times \text{eq. wt. CaCO}_3}{\text{mL}_{\text{sample}}}$$

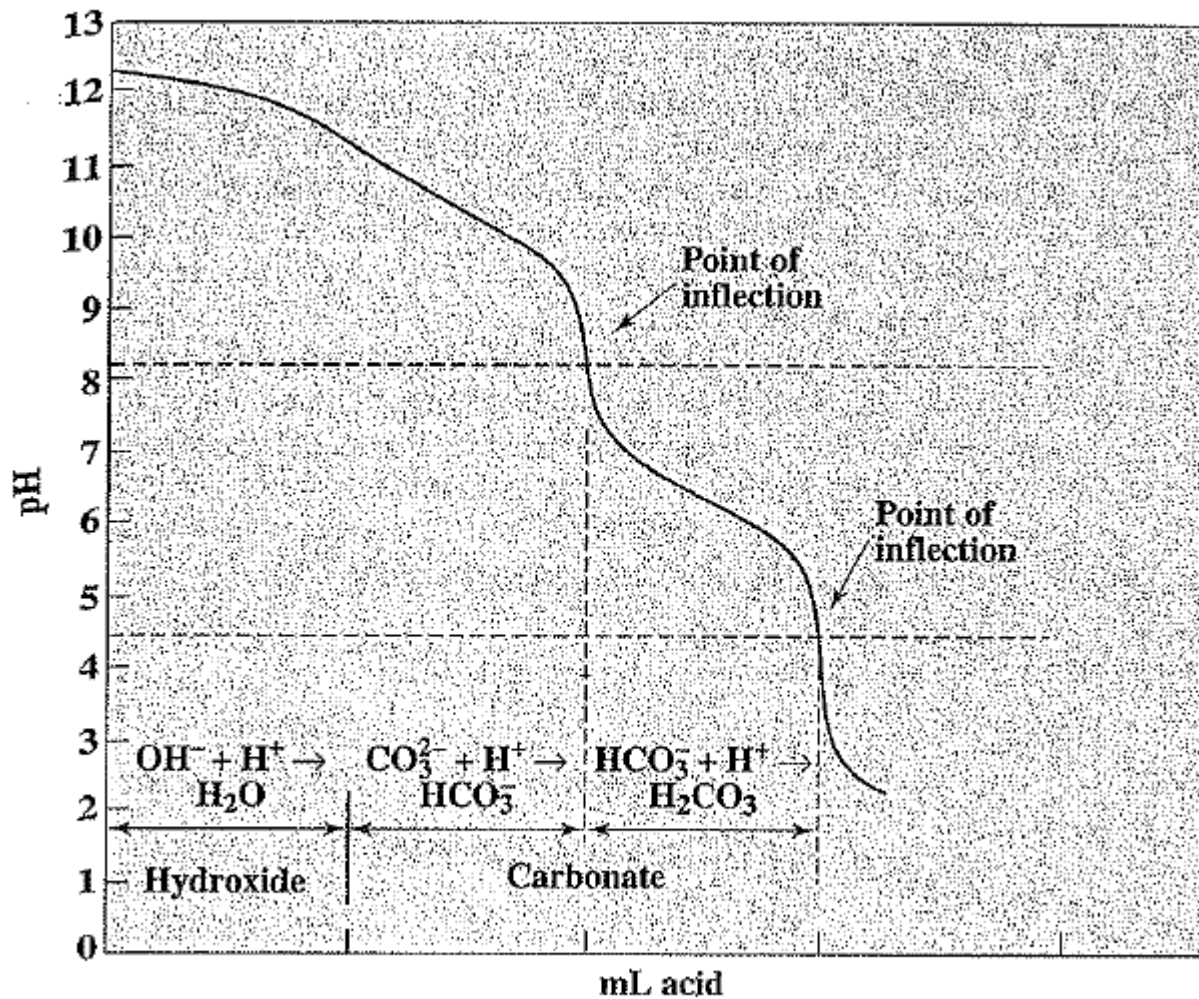


Figure 18.1
Titration curve for a hydroxide-carbonate mixture.

Methods of expressing alkalinity

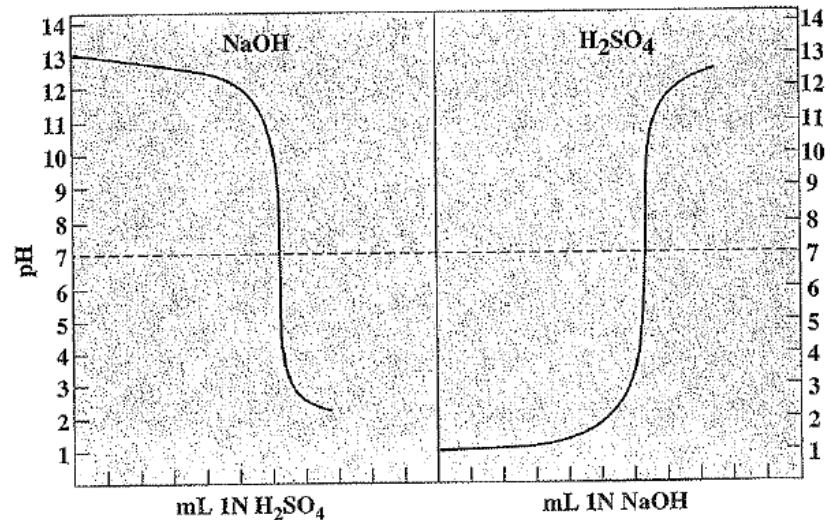
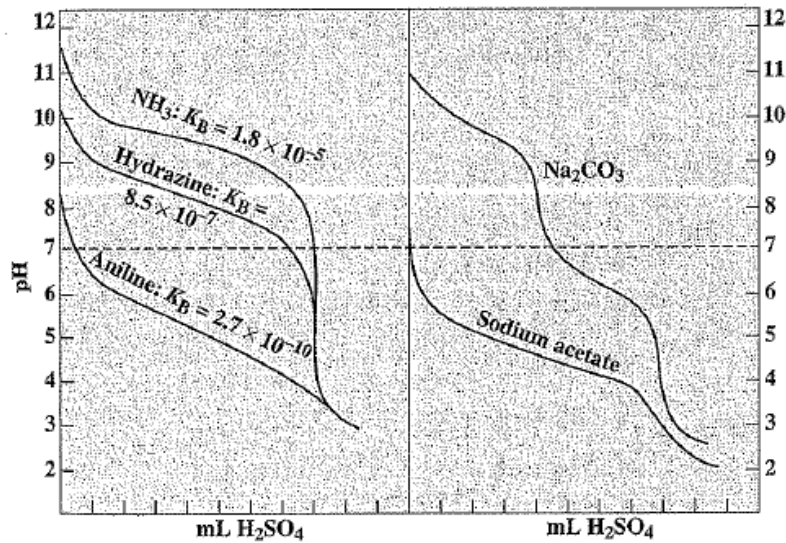


Figure 4.7
Titration curves for strong bases and acids.

Figure 4.9
Titration curves for weak bases and for salts of weak acids.

Phenolphthalein and Total Alkalinity

@ pH 10 all the hydroxide ions are neutralized

@ pH 8.3 carbonate converted to bicarbonate

Titration till phenolphthalein end point →

Phenolphthalein alkalinity

Total alkalinity → titration till pH 4.5

Conversion till carbonic acid H_2CO_3

$$\text{Phenol. alk.} = (\text{mL } 0.020 \text{ N H}_2\text{SO}_4 \text{ to pH } 8.3) \frac{1000}{\text{mL sample}} \quad (18.4)$$

$$\text{Total alk.} = \text{total mL } 0.020 \text{ N H}_2\text{SO}_4 \text{ to pH } \begin{cases} 5.0 \\ 4.8 \\ 4.6 \\ 4.0 \end{cases} \times \frac{1000}{\text{mL sample}} \quad (18.5)$$

Hydroxide, Carbonate and Bicarbonate Alaklinity

1. Calculation from alkalinity measurements
2. Calculation from alkalinity and pH measurement
3. Calculation from equilibrium equations (carbonic acid)

1. Calculation from alkalinity measurements

- * Based on assumptions and total/phenolphthalein alkalinity measurements
- * Assumption: Hydroxide and bicarbonate alkalinities cannot be present at the same time (incorrect but rough estimate)

Five possible situations :

1. Hydroxide only
2. Carbonate only
3. Hydroxide and Carbonate
4. $\text{CO}_3^{=}$ and HCO_3^-
5. HCO_3^-

@pH 8.3 neutralization of hydroxides are completed.

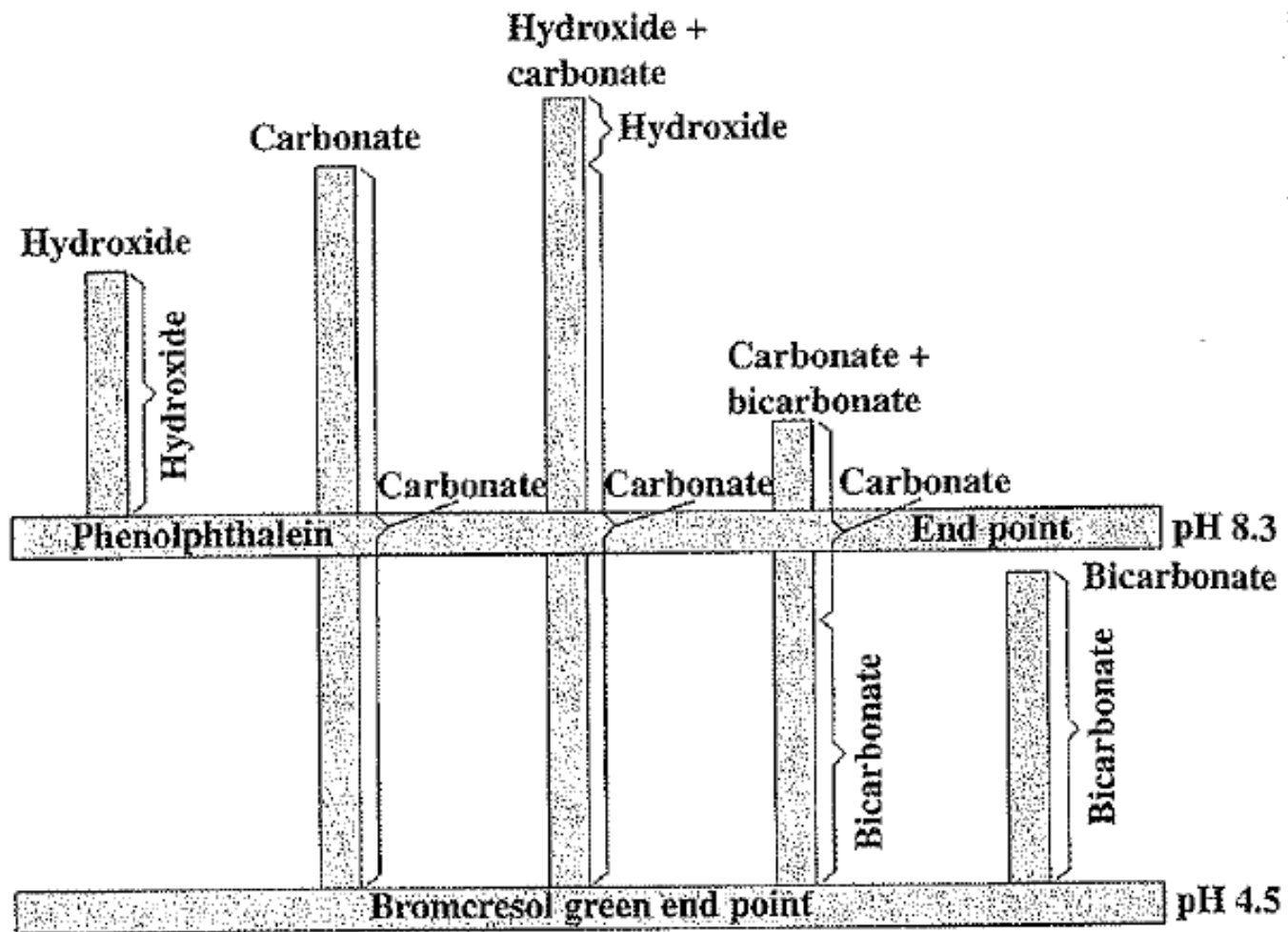


Figure 18.2

Graphical representation of titration of samples containing various forms of alkalinity.

Hydroxide alkalinity

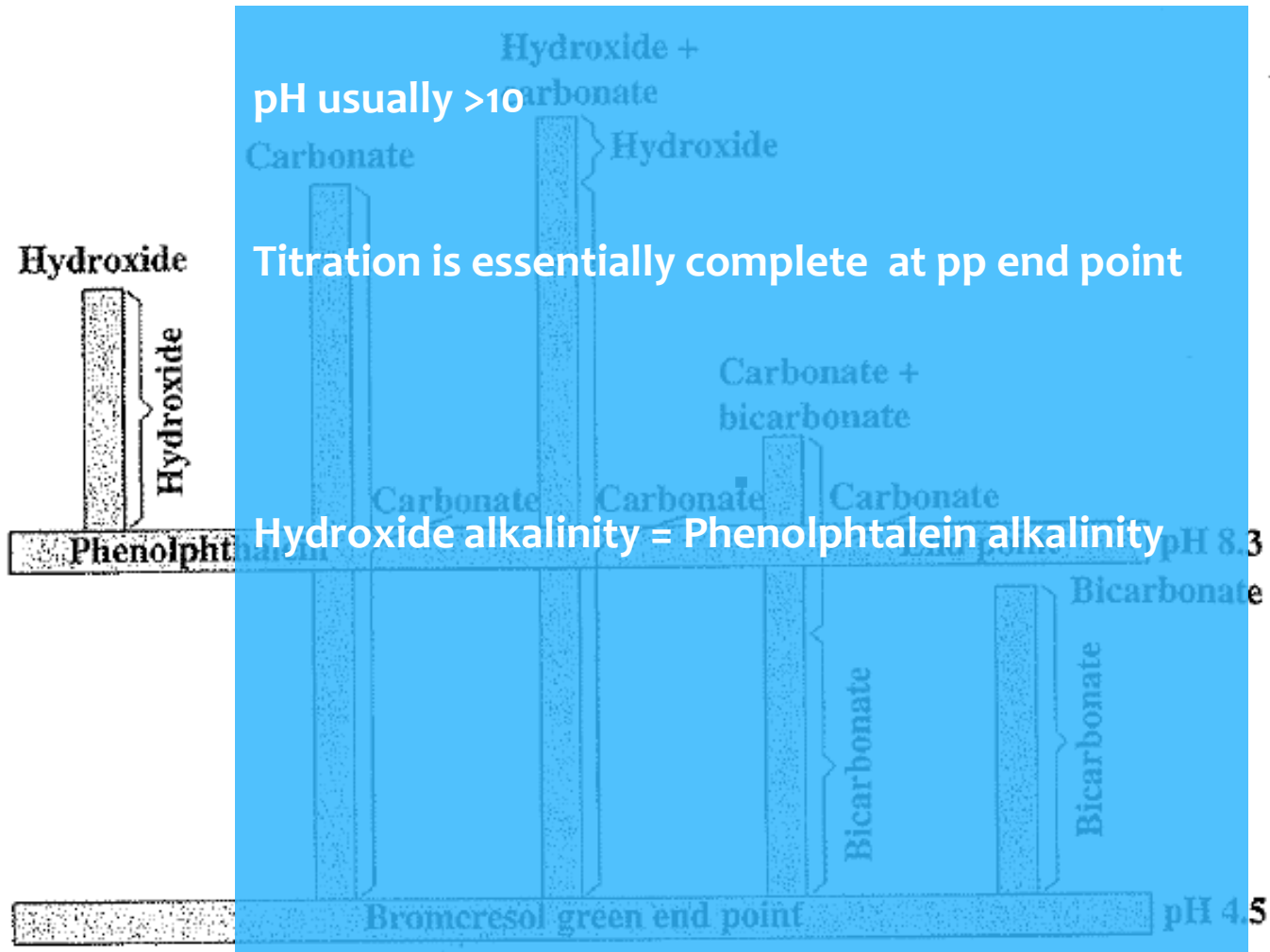


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Graphical representation of titration of samples containing various forms of alkalinity.

Carbonate only

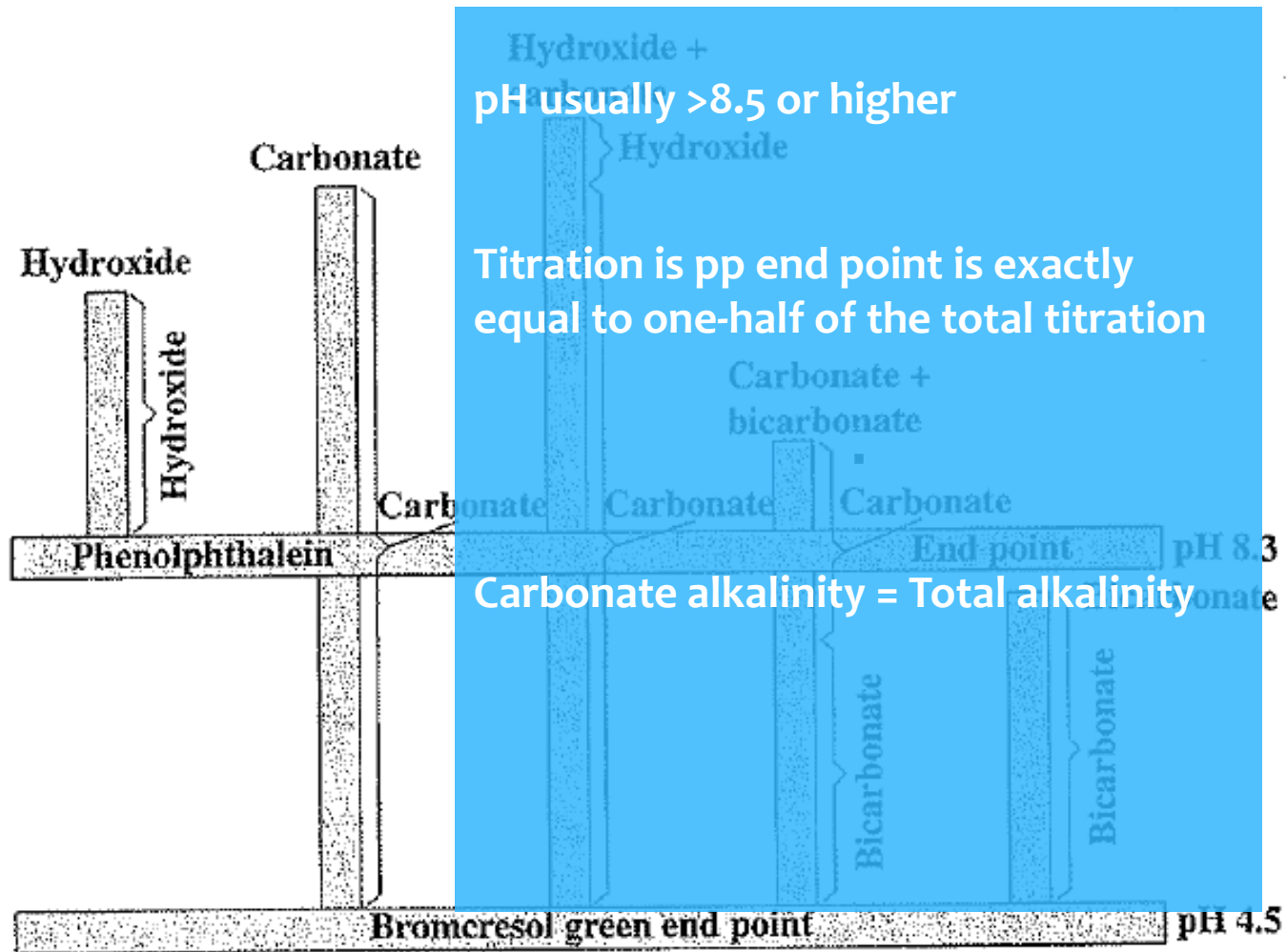


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Hydroxide-carbonate

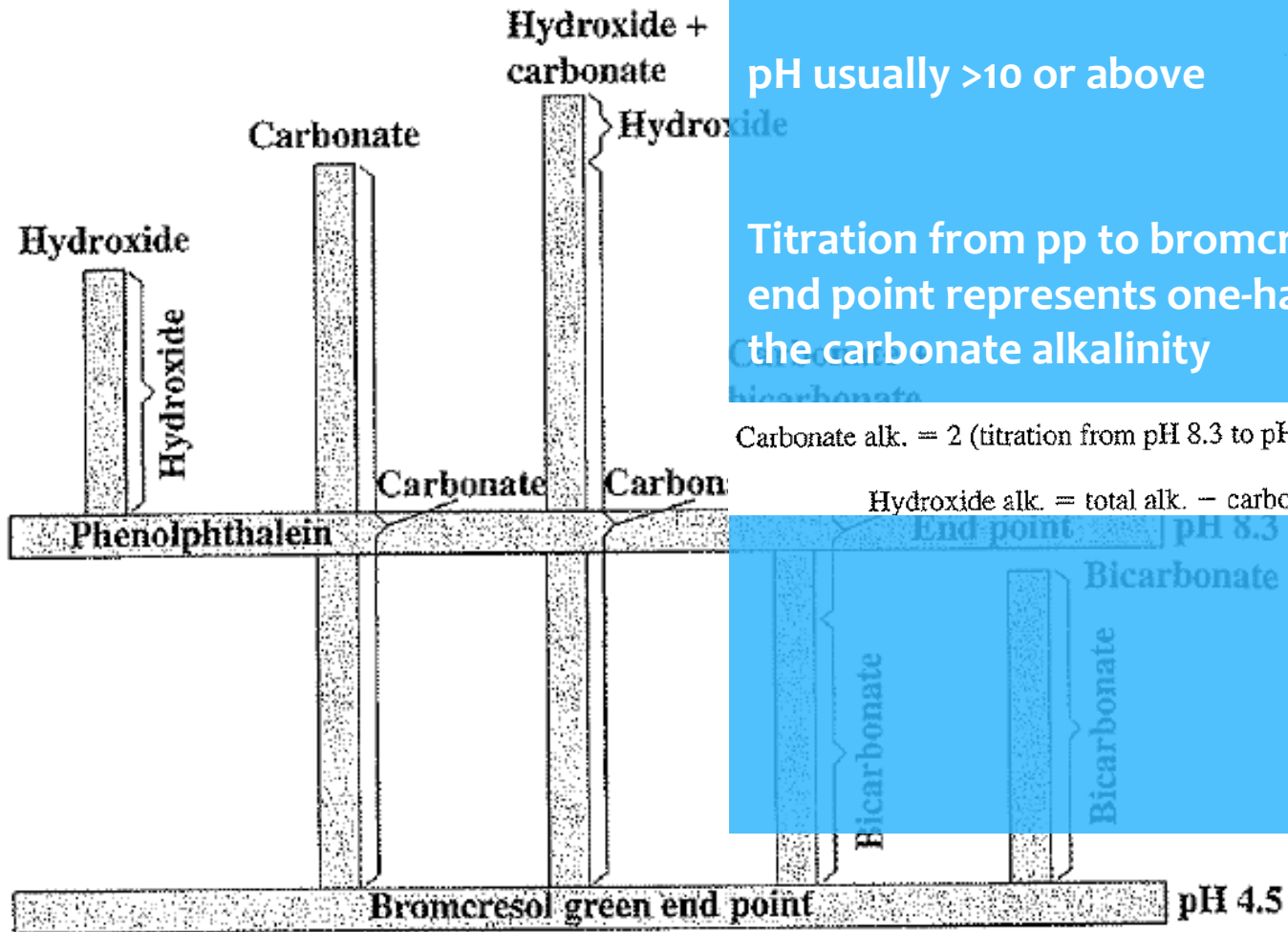
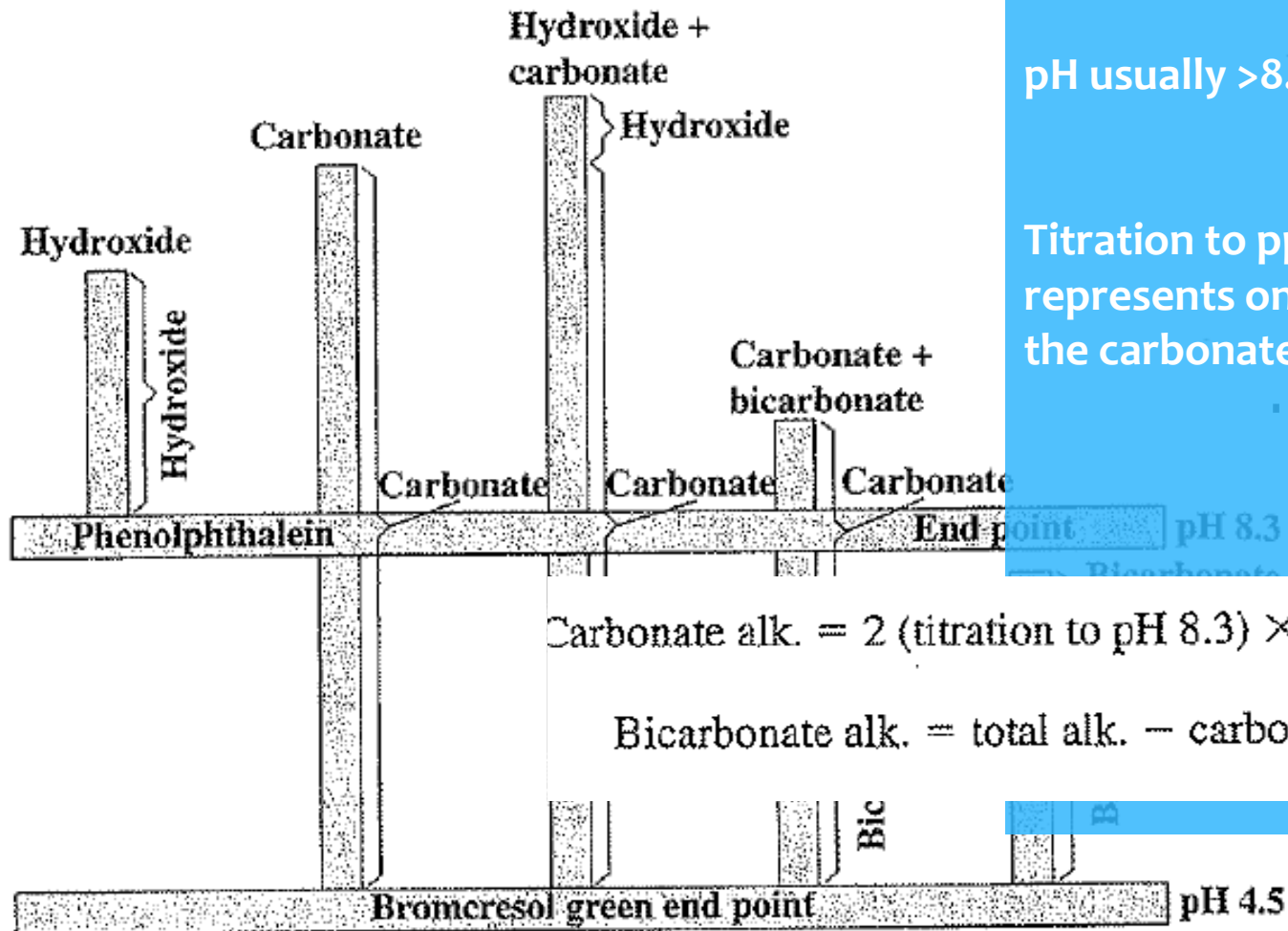


Figure 18.2

Graphical representation of titration of samples containing various forms of alkalinity.

Carbonate-bicarbonate



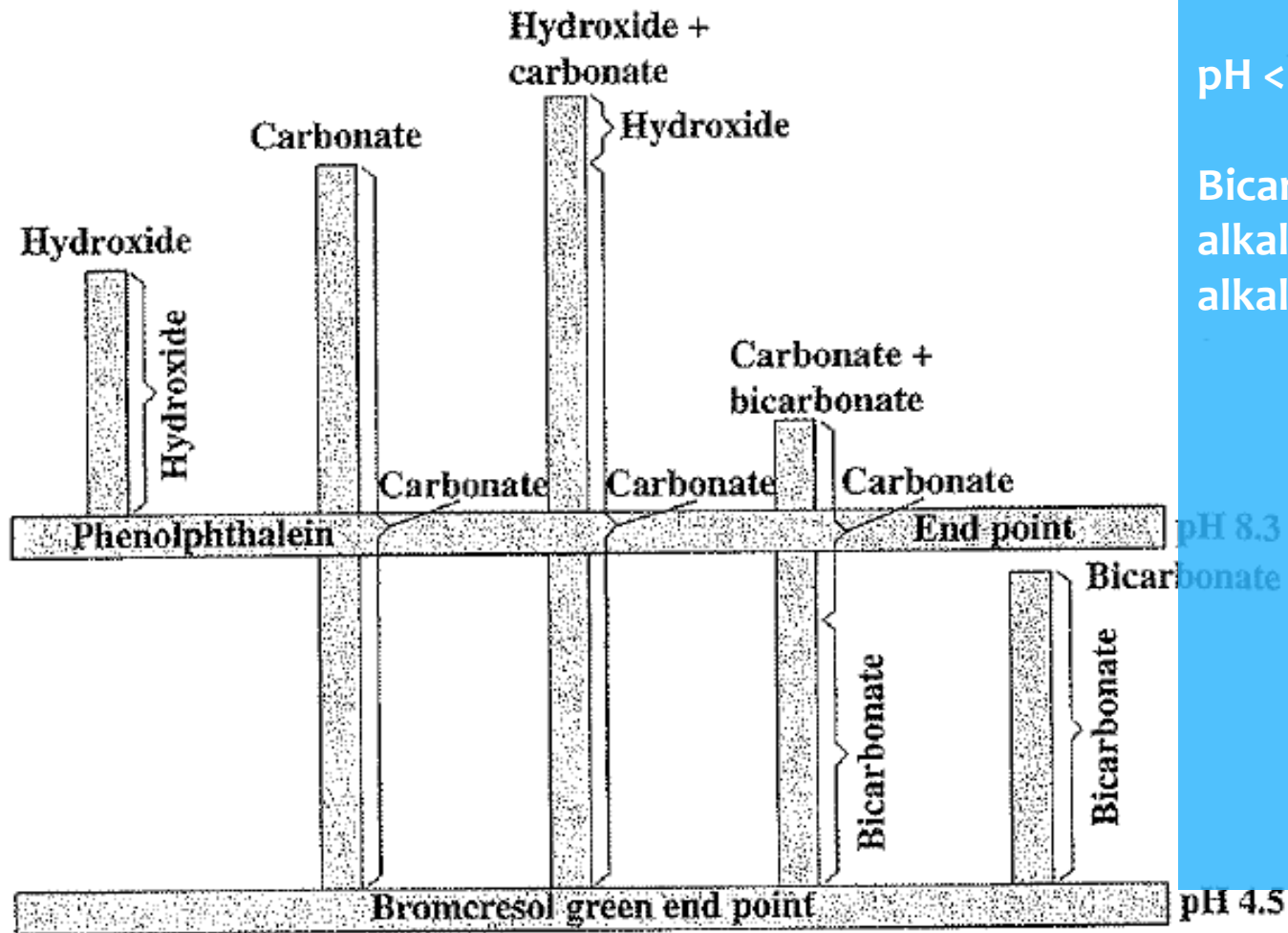
pH usually >8.3 and <11

Titration to pp end point represents one-half of the carbonate alkalinity

Figure 18.2

Graphical representation of titration of samples containing various forms of alkalinity.

Bicarbonate



pH < 8.3

Bicarbonate
alkalinity = total
alkalinity

pH 8.3
Bicarbonate

pH 4.5

Figure 18.2

Graphical representation of titration of samples containing various forms of alkalinity.

2. Calculation from alkalinity + pH measurements

- * Should measure
 - * pH
 - * Total alkalinity
 - * Phenolphthalein alkalinity
- * Calculate hydroxide, carbonate, bicarbonate alkalinity

2. Calculation from alkalinity + pH measurements

- * First calculate OH alkalinity from pH measurement

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \quad (18.6)$$

$$\text{Hydroxide alk.} = 50,000 \times 10^{(\text{pH} - \text{p}K_w)} \quad (18.7)$$

At 25°C, $\text{p}K_w = 14.00$. However, it varies from 14.94 at 0°C to 13.53 at 40°C.

2. Calculation from alkalinity + pH measurements

- * Second, make use of the principles of the first procedure to calculate carbonate and bicarbonate alkalinity

$$\text{Carbonate alk.} = 2 (\text{phenol. alk.} - \text{hydroxide alk.}) \quad (18.8)$$

- * Titration from pH 8.3 to 4.5 measures the remaining one half of the carbonate + bicarbonate.

- * or

$$\text{Bicarbonate alk.} = \text{total alk.} - (\text{carbonate alk.} + \text{hydroxide alk.}) \quad (18.9)$$

Alkalinity and acidity are based on the “carbonate system” .

$$[\text{Alk.}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{=}] + [\text{OH}^-] - [\text{H}^+]$$

(mol/L of H^+ that can be neutralized)

$$(\text{Alk.}) = (\text{HCO}_3^-) + (\text{CO}_3^{=}) + (\text{OH}^-) - (\text{H}^+)$$

(eq/L of H^+ that can be neutralized)

$$\text{Alk. In mg/L as CaCO}_3 = (\text{Alk.}) \times \text{EW}_{\text{CaCO}_3}$$

Example :

$$\text{CO}_3^{=} = 20 \text{ g/m}^3$$

$$\text{HCO}_3^- = 488 \text{ g/m}^3$$

$$\text{OH}^- = 0.17 \text{ g/m}^3$$

$$\text{Alk.} = ?$$

Ion	MW (g/mole)	EW (g/eq)	(eq/m ³)
$\text{CO}_3^{=}$	60	30	$20/30=0.67$
HCO_3^-	61	61	$488/61=8$
OH^-	17	17	$0.17/17=0.01$

$$[\text{H}^+][\text{OH}^-] = K_w$$

$$(\text{OH}^-)(\text{H}^+) = K_w$$

$$\begin{aligned}[\text{H}^+] &= 10^{-14} / (0,01 \times 1/1000 \times 1 \text{ mol/eq}) \\ &= 10^{-9} \text{ mol/L} = 10^{-9} \text{ eq/L} = 10^{-6} \text{ eq/m}^3\end{aligned}$$

$$[\text{Alk.}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{=}] + [\text{OH}^-] - [\text{H}^+]$$

$$\begin{aligned}(\text{Alk.}) &= 8,00 + 0,67 + 0,01 - 10^{-6} \\ &= 8,68 \text{ eq/m}^3\end{aligned}$$

$$(8,68 \times 10^{-3} \text{ eq/L}) \times (50000 \text{ mg/eq}) = 434 \text{ mg/L as CaCO}_3$$

Expressing in terms of CaCO_3

Species A

$$\text{mg/L as CaCO}_3 = (\text{mg/L A})(\text{EW}_{\text{CaCO}_3} / \text{EW}_A)$$

Example : 10 mg/L Mg^{2+}

$$\text{Mg}^{+2} = 24,3 \text{ mg/L} \quad \text{EW}_{\text{Mg}^{+2}} = 24,3/2=12,15$$

Conc of Mg^{+2} as CaCO_3

$$(10 \text{ mg/L}) \times ((5000 \text{ mg/eq}) / (12150 \text{ mg/eq Mg}^{+2}))$$

$$= 41,15 \text{ mg/L as CaCO}_3$$

3. Calculation from equilibrium reactions

$$[\text{H}^+] + \frac{\text{alkalinity}}{50,000} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (18.10)$$

$$\frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (18.11)$$

$$\text{Carbonate alkalinity (mg/L as CaCO}_3) = \frac{50,000[(\text{alkalinity}/50,000) + [\text{H}^+] - (K_w/[\text{H}^+])]}{1 + ([\text{H}^+]/2K_{A2})} \quad (18.12)$$

$$\text{Bicarbonate alkalinity (mg/L as CaCO}_3) = \frac{50,000[(\text{alkalinity}/50,000) + [\text{H}^+] - (K_w/[\text{H}^+])]}{1 + (2K_{A2}/[\text{H}^+])} \quad (18.13)$$

Application of alkalinity data

- * **Chemical coagulation:** excess alkalinity should be present
- * **Water softening:** important in calculating lime and soda ash requirements
- * **Biological processes**
- * **Industrial wastewaters:** Many municipalities prohibit caustic alkalinity to sewers
 - * ISKI requires $6 < \text{pH} < 12$

pH changes during aeration of water

- * Common purpose of aeration is to strip
 - * Carbondioxide \rightarrow pH \uparrow
 - * Ammonia
 - * VOCs
- * Air content 0,035 % by volume CO₂
- * Henry 's constant : 1500 mg/L.atm

Equilibrium conc.for CO₂ = 0,00035 x 1500 = 0,45 mg/L

$$K_{A1} = [H^+][HCO_3^-] / [H_2CO_3]$$

If alkalinity = 100 mg/L

Aerated until equilibrium of CO₂ in air \rightarrow pH=8,6

pH changes in the presence of algal blooms

- * Algae use CO_2 in photosynthesis.
- * Algae can reduce CO_2 conc. below its equilibrium concentrations.
- * During algal blooms pH 10 can be seen
- * Algae can continue to extract CO_2 until inhibitory pH (10-11)
- * As pH increase alkalinity forms change
- * Total alkalinity remains constant unless CaCO_3 precipitation occurs

Boiler waters

- * Carbon dioxide is insoluble in boiling water and removed with steam. \rightarrow pH \uparrow \rightarrow shift of alkalinity from bicarbonate to carbonate, and carbonate to hydroxide \rightarrow CaCO_3 precipitate