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CEE 680: Water Chemistry

Lecture #20

Dissolved Carbon Dioxide: Closed Systems II & Alkalinity

(Stumm & Morgan, Chapt.4)

Benjamin; Chapter 5.4 & 7

Alkalinity

- Northampton MA
  - From Homework #1

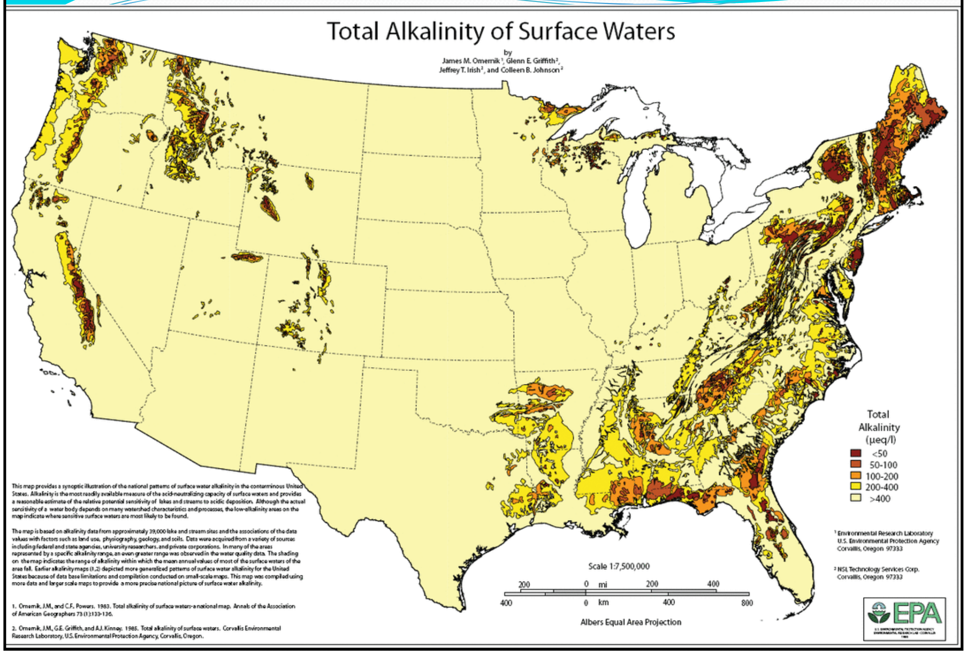
Constituent	Concentration	Units
Turbidity	0.59	NTU
TDS	29	mg/L
Color	10	Color units
Odor	1	TON
pH	6.75	Log units
Total Alkalinity	13	mg-$CaCO_3$/L
Total Hardness	20	mg-$CaCO_3$/L
Calcium	6.7	mg/L
Magnesium	0.89	mg/L
Aluminum	<0.05	mg/L
Potassium	<1	mg/L
Sodium	5.0	mg/L
Iron	<0.05	mg/L
Manganese	0.016	mg/L
Sulfate	5.9	mg/L
Chloride	3.0	mg/L
Silver	<0.005	mg/L
Copper	<0.01	mg/L
Zinc	<0.05	mg/L
TOC	3	mg/L

13 mg/L as $CaCO_3$

0.26 meq/L

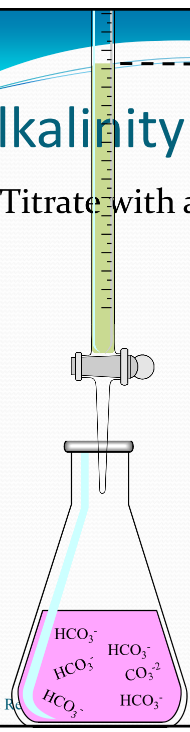
260 µeq/L

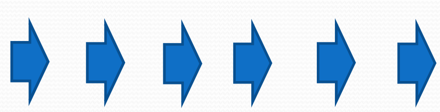
https://www.usgs.gov/special-topic/water-science-school/science/alkalinity-and-water?qt-science_center_objects=0#qt-science_center_objects

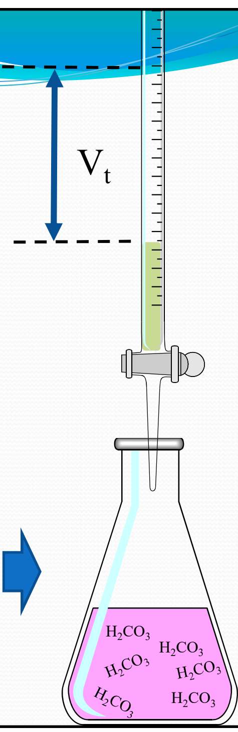


Alkalinity Test

- Titrate with a strong acid (e.g., HCl)







$$H^+ + \mathbf{HCO_3^-} \rightarrow \mathbf{H_2CO_3^-}$$

$$2H^+ + \mathbf{CO_3^{-2}} \rightarrow \mathbf{H_2CO_3^-}$$

Alkalinity

- Alkalinity: ability of a water to neutralize strong acids
  - a form of Acid Neutralizing Capacity (ANC)
  - Interpretation in most natural waters:
    - $Alk_{tot} = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-] - [H^+]$
      - Net deficiency of protons with respect to CO_2 — H_2CO_3
      - Alk = 0 for a pure solution of carbon dioxide; therefore, CO_2 does not add alkalinity: $CO_2(aq)+OH^- = HCO_3^-$
    - $Alk_{tot} = (\alpha_1 + 2\alpha_2)C_T + [OH^-] - [H^+]$
  - Measurement by titration with a strong acid back to the pH of a pure CO_2 solution (about 4.5)

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Acidity

- Acidity: abilility of a water to neutralize strong bases
  - a form of Base Neutralizing Capacity (BNC)
  - Interpretation in most natural waters
    - $Acy_{tot} = 2[H_2CO_3] + [HCO_3^-] + [H^+] - [OH^-]$
      - Net excess of protons with respect to CO_3^{-2}
      - Acy = 0 for a pure solution of carbonate; therefore, Na_2CO_2 does not add acidity: $Na_2CO_2 + H^+ = HCO_3^- + 2Na^+$
    - $Acy_{tot} = (2\alpha_0 + \alpha_1)C_T + [H^+] - [OH^-]$
  - Measurement by titration with a strong base back to the pH of a pure CO_3^{-2} solution (about 10.7)

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Acidity & Alkalinity (cont.)

- Summation
  - $Alk_{tot} + Acy_{tot}$
    - $= ([HCO_3^-] + 2[CO_3^{-2}] + [OH^-] - [H^+]) + (2[H_2CO_3] + [HCO_3^-] + [H^+] - [OH^-])$
    - $= 2[H_2CO_3] + 2[HCO_3^-] + 2[CO_3^{-2}]$
    - $=2C_T$
  - therefore, you can determine C_T from the two titrations
- Since Alkalinity is not affected by addition of CO_2 it is considered a conservative substance in "open systems"
  - e.g., loss of CO_2 to the atmosphere does not affect alkalinity either

Other Alkalinity Species

- In sea water we use:
  - $Alk_{tot} = [HCO_3^-] + 2[CO_3^{-2}] + [B(OH)_4] + [HPO_4^{-2}] + [H_3SiO_4] + [MgOH^-] + [OH^-] - [H^+]$

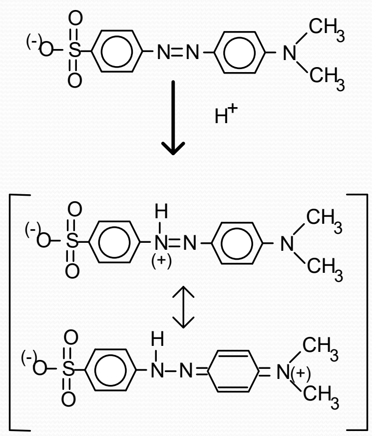
Species	pKa	Average Conc. (M)	Equilibria
Carbonates	10.3/6.4	$1x10^{-3}$	$CO_3^{-2} + 2H^+ = HCO_3^- + H^+ = H_2CO_3$
Silicates	9.8	$2x10^{-4}$	$H_3SiO_4 + H^+ = H_4SiO_4$
Organics	3 to 10	$1x10^{-4}$	$R\text{-}COO^- + H^+ = R\text{-}COOH$
Borates	9.2	$1x10^{-6}$	$B(OH)_4^- + H^+ = B(OH)_3 + H_2O$
Ammonia	9.2	$2x10^{-6}$	$NH_4OH + H^+ = NH_4^+ + H_2O$
Iron	6.0/4.6	$2x10^{-6}$	$Fe(OH)_4^- + 3H^+ = Fe(OH)_2^+ + H^+ = Fe(OH)^{+2}$
Aluminum	8.0/5.7	$2x10^{-6}$	$Al(OH)_4^- + 2H^+ = Al(OH)_3 + H^+ = Al(OH)_2^+$
	4.3/5.0		$Al(OH)_2^+ + 2H^+ = Al(OH)^{+2} + H^+ = Al^{+3}$
Phosphates	7.2	$7x10^{-7}$	$HPO_4^{-2} + H^+ = H_2PO_4^-$
Hydroxide	14.0	$2x10^{-7}$	$OH^- + H^+ = H_2O$
Copper	9.8/7.3	$1x10^{-7}$	$Cu(OH)_3^- + 3H^+ = Cu(OH)^+ + H^+ = Cu^+ + H_2O$
Nickel	6.9	$2x10^{-8}$	$Ni(OH)_2 + H^+ = NiOH^+$
Cadmium	7.6	$1x10^{-8}$	$Cd(OH)^+ + H^+ = Cd^{+2} + H_2O$
Lead	6.2	$1x10^{-8}$	$Pb(OH)^+ + H^+ = Pb^{+2} + H_2O$
Sulfides	7.0	variable	$HS^- + H^+ = H_2S$
Zinc	6.1/9.0	variable	$Zn(OH)_2 + 2H^+ = Zn(OH)^+ + H_3O^+ = Zn^{+2} + 2H_2O$

Chemical species which may contribute to alkalinity

See also, Table IX in Faust & Aly, 1981

Methyl Orange

- used as a colorimetric indicator of the final alkalinity titration endpoint
  - changes color at about pH 4.5
  - where all carbonates are as H_2CO_3
  - f=2

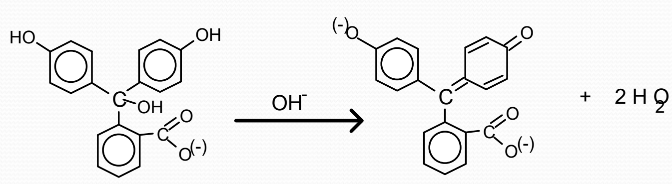


Yellow

Red

Phenolphthalein

- used as a colorimetric indicator of alkalinity and acidity first endpoint
  - changes color at about pH 8.3
  - pH signifies loss of OH^- and where all carbonates are as HCO_3^-
  - at f=1, and g=1



Colorless Red

Alkalinity procedures (cont.)

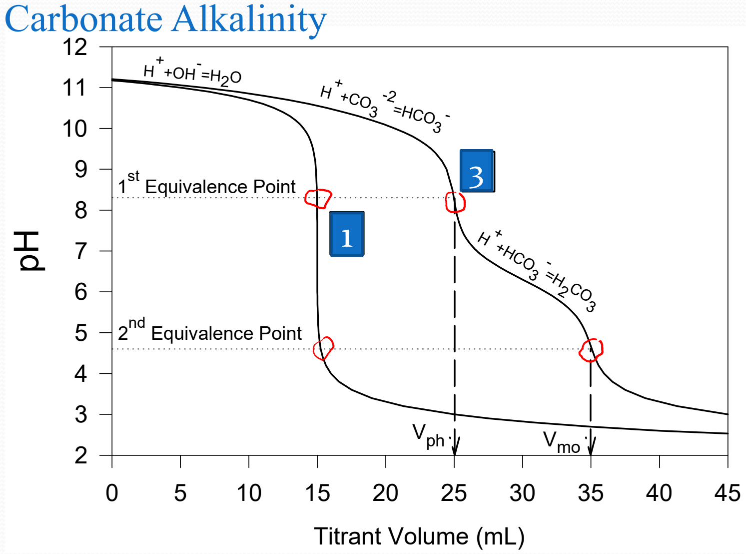
- calculations
  - $Equ_t = Equ_s$
  - $V_tN_t = V_sN_s$
  - $N_s = V_tN_t / V_s$
- Sliding endpoint depending on concentration

Alkalinity (mg/L)	Potentiometric (pH)	Colorimetric (from greenish blue to)
30	4.9	light blue & lavender
150	4.6	light pink
500	4.3	red

Examples

- Titrate 1 L of each with 0.100 M HCl
  - Determine the pH at various points in the titration
- Solution #1
  - 1.5 mM of NaOH
- Solution #2
  - 1.5 mM of NaOH, plus 1.0 mM NaOCl
- Solution #3
  - 1.5 mM of NaOH, plus 1.0 mM Na_2CO_3

Acid Titration Curve for a Water Containing Hydroxide and Carbonate Alkalinity



Alkalinity: Chemical Interpretation

- At the phenolphthalein endpoint (Alk_{ph}), the following has occurred:
  - $H^+ + \mathbf{OH^-} \rightarrow H_2O$
  - $H^+ + \mathbf{CO_3^{-2}} \rightarrow \mathbf{HCO_3^-}$
- Then at the methyl orange endpoint (Alk_{mo}):
  - $H^+ + \mathbf{HCO_3^-} \rightarrow H_2CO_3 \leftrightarrow CO_2 + H_2O$
- Units:
  - equ/L
  - or more commonly, **mg/L as $CaCO_3$**
    - 1 equ/L = 50,000 mg/L as $CaCO_3$

Types of Alkalinity

- Speciation based on carbonate system
  - $Alk_{OH} = 50{,}000[OH^-] = 50{,}000(10^{pHi-14})$
  - $Alk_{HCO3} = 50{,}000[HCO_3^-]$
  - $Alk_{CO3} = 100{,}000[CO_3^{-2}]$

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Scheme for Alk determination

- If $Alk_{ph} > 0.5 * Alk_{mo}$
  - $Alk_{OH} = 2*Alk_{ph} - Alk_{mo}$
  - $Alk_{CO3} = 2(Alk_{mo} - Alk_{ph})$
  - $Alk_{HCO3} = 0$
- If $Alk_{ph} \leq 0.5 * Alk_{mo}$
  - $Alk_{OH} = 0$
  - $Alk_{CO3} = 2*Alk_{ph}$
  - $Alk_{HCO3} = Alk_{mo} - 2*Alk_{ph}$
- Where:
  - $Alk_{ph} = 50{,}000 V_{ph} N_t / V_s$
  - $Alk_{mo} = 50{,}000 V_{mo} N_t / V_s$

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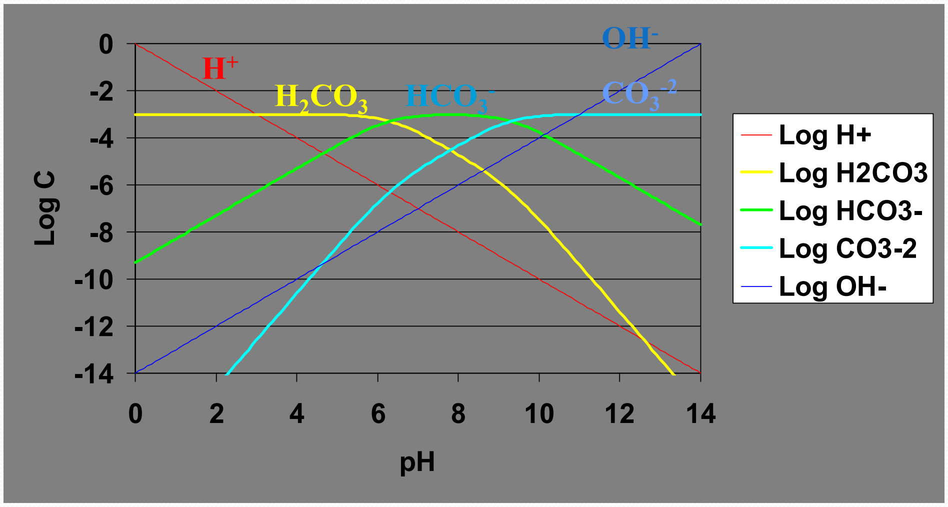
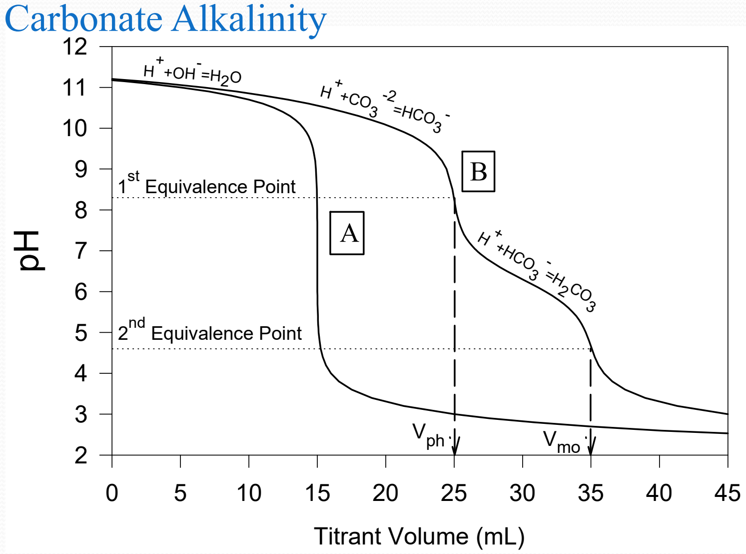
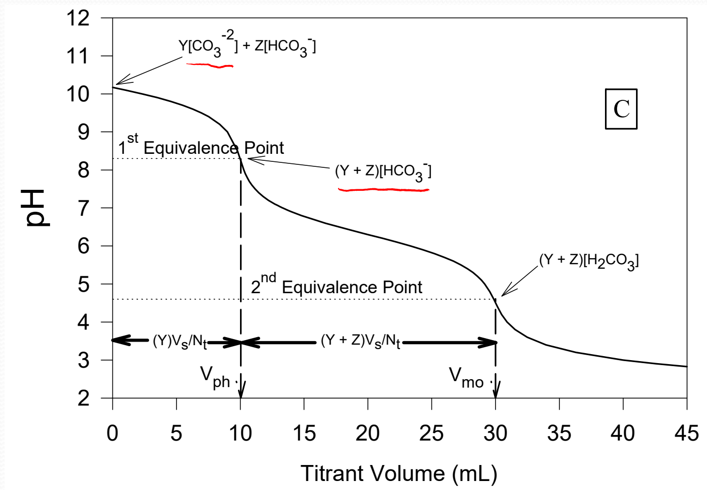
Carbonate System ($C_T=10^{-3}$)



Acid Titration Curve for a Water Containing Hydroxide and Carbonate Alkalinity



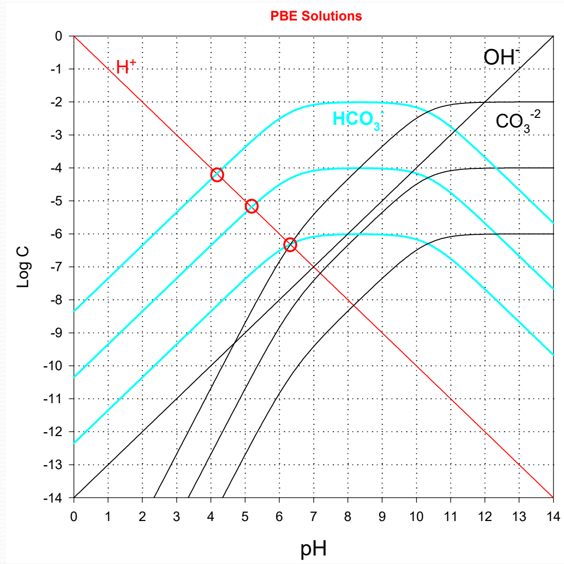
Acid Titration Curve for a Water Containing Carbonate and Bicarbonate Alkalinity



Alkalinity & titrations (cont.)

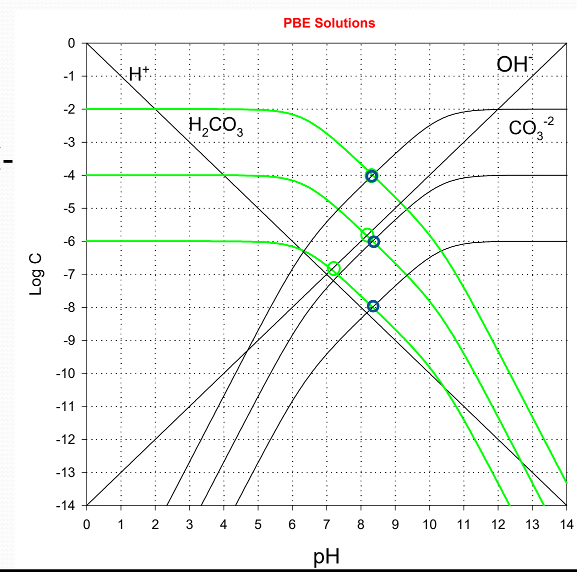
- Relationship between chemistry, titration and buffer intensity
  - See Stumm & Morgan, Figure 4.1 (pg. 154)
- Impact of C_T on titration endpoints
  - Refer to Benjamin, Figure 5.10
    - Also: Stumm & Morgan, Figure 4.3 (pg.157) and Pankow's Figure 9.2 (pg. 169)
- Conservation of Alkalinity
  - Stumm & Morgan, Figures 4.7 and 4.10 (pgs. 167 and 177)

Pure H_2CO_3: f=0

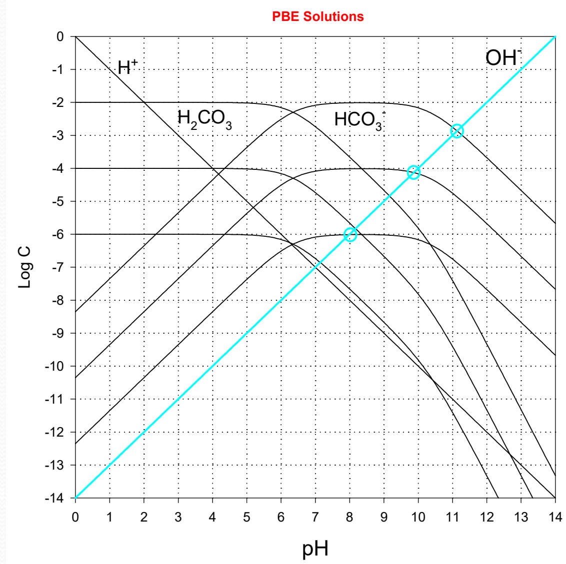


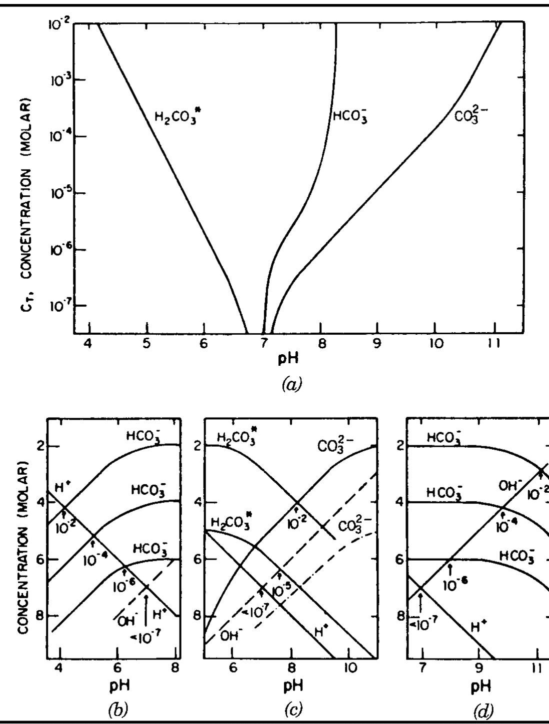
Pure HCO_3^-: f=1

- Solution to PBE shifts from H2CO3-CO3-2 intersection (blue o circles) to H2CO3-OH- intersection (green o circles) as CT drops



Pure CO_3^{-2}: f=2





Stumm & Morgan
Figure 4.3; pg. 157

- To next lecture