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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 $CaCO_3$

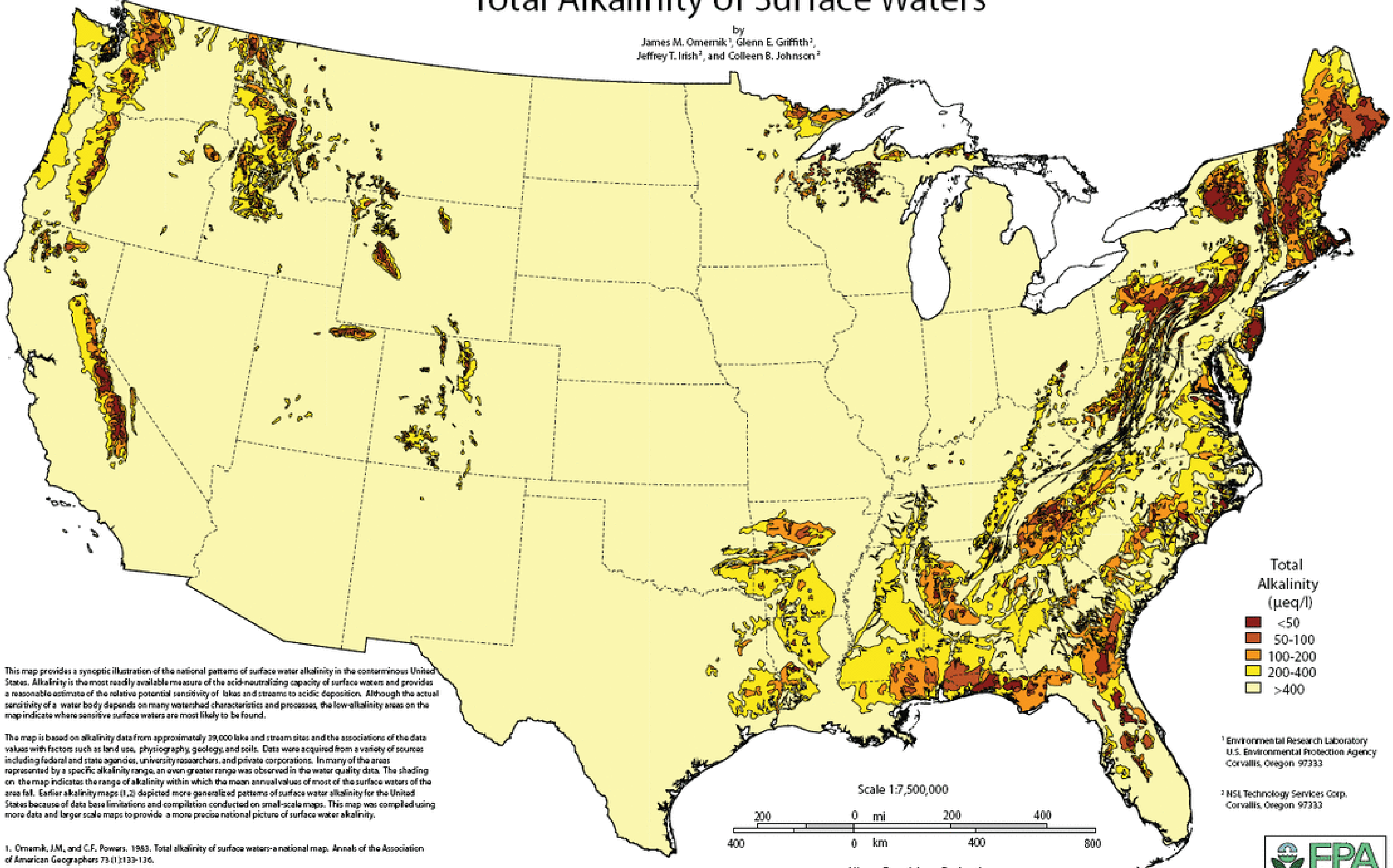
0.26 meq/L

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

Total Alkalinity of Surface Waters

by
James M. Omernik[1], Glenn E. Griffith[2],
Jeffrey T. Irish[2], and Colleen B. Johnson[2]



This map provides a synoptic illustration of the national patterns of surface water alkalinity in the conterminous United States. Alkalinity is the most readily available measure of the acid-neutralizing capacity of surface waters and provides a reasonable estimate of the relative potential sensitivity of lakes and streams to acidic deposition. Although the actual sensitivity of a water body depends on many watershed characteristics and processes, the low-alkalinity areas on the map indicate where sensitive surface waters are most likely to be found.

The map is based on alkalinity data from approximately 39,000 lake and stream sites and the associations of the data values with factors such as land use, physiography, geology, and soils. Data were acquired from a variety of sources including federal and state agencies, university researchers, and private corporations. In many of the areas represented by a specific alkalinity range, an even greater range was observed in the water quality data. The shading on the map indicates the range of alkalinity within which the mean annual values of most of the surface waters of the area fall. Earlier alkalinity maps (1,2) depicted more generalized patterns of surface water alkalinity for the United States because of data base limitations and compilation conducted on small-scale maps. This map was compiled using more data and larger scale maps to provide a more precise national picture of surface water alkalinity.

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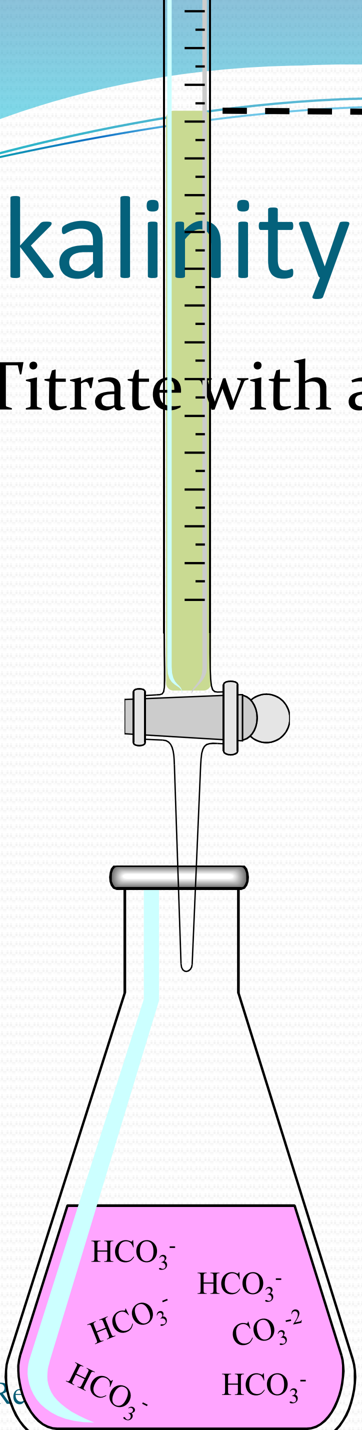
1. Omernik, J.M., and C.F. Powers. 1983. Total alkalinity of surface waters-a national map. Annals of the Association of American Geographers 73 (1):133-136.

2. Omernik, J.M., G.E. Griffith, and A.J. Kinney. 1985. Total alkalinity of surface waters. Corvallis Environmental Research Laboratory, U.S. Environmental Protection Agency, Corvallis, Oregon.

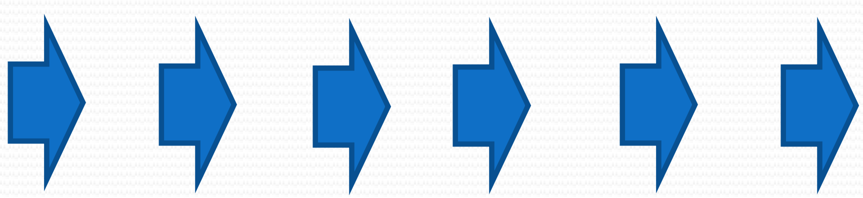
Alkalinity Test

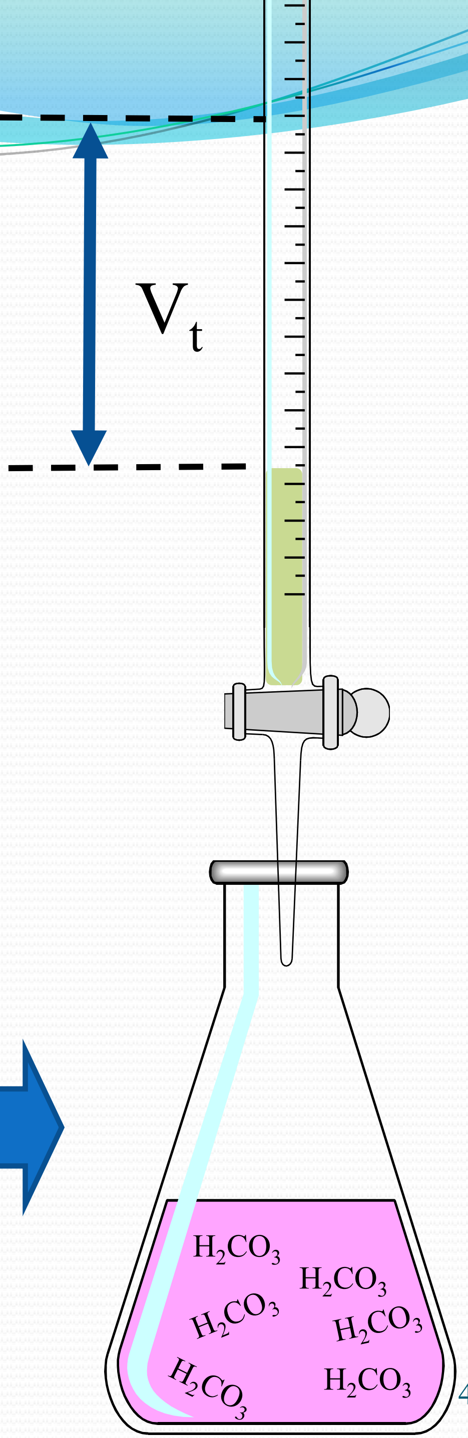
- Titrate with a strong acid (e.g., HCl)



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

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





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
      - 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)

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)

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

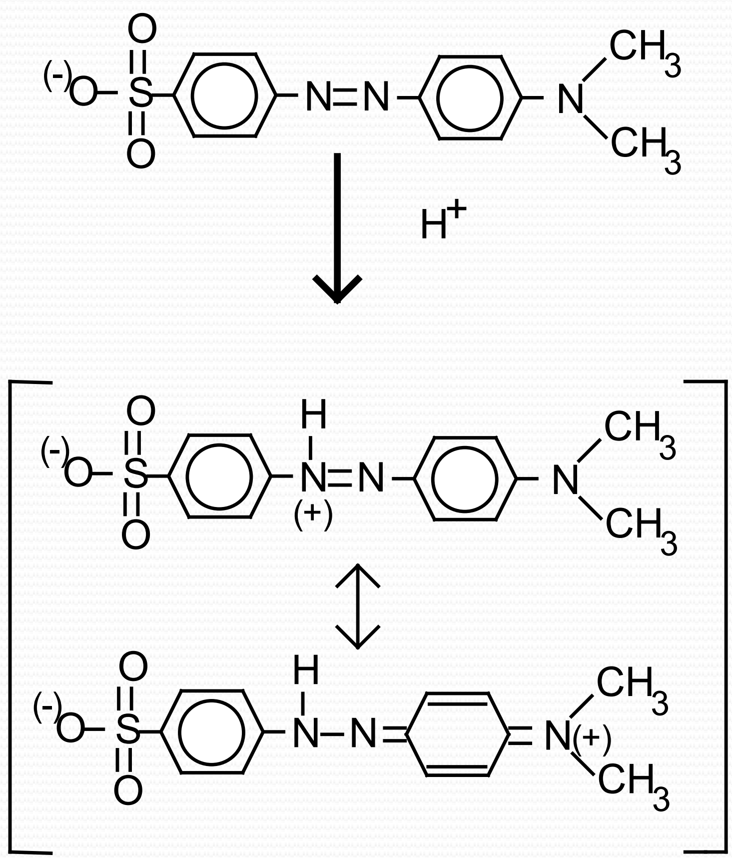
Species	pKa	Average Conc. (M)	Equilibria
Carbonates	10.3/6.4	$1x10^{-3}$	$CO_3^{-2} + 2H^+ = HCO_3^- + H^+ = H_2CO_3$
Silicates	9.8	$2x10^{-4}$	$H_3SiO_4 + H^+ = H_4SiO_4$
Organics	3 to 10	$1x10^{-4}$	$R\text{-}COO^- + H^+ = R\text{-}COOH$
Borates	9.2	$1x10^{-6}$	$B(OH)_4^- + H^+ = B(OH)_3 + H_2O$
Ammonia	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

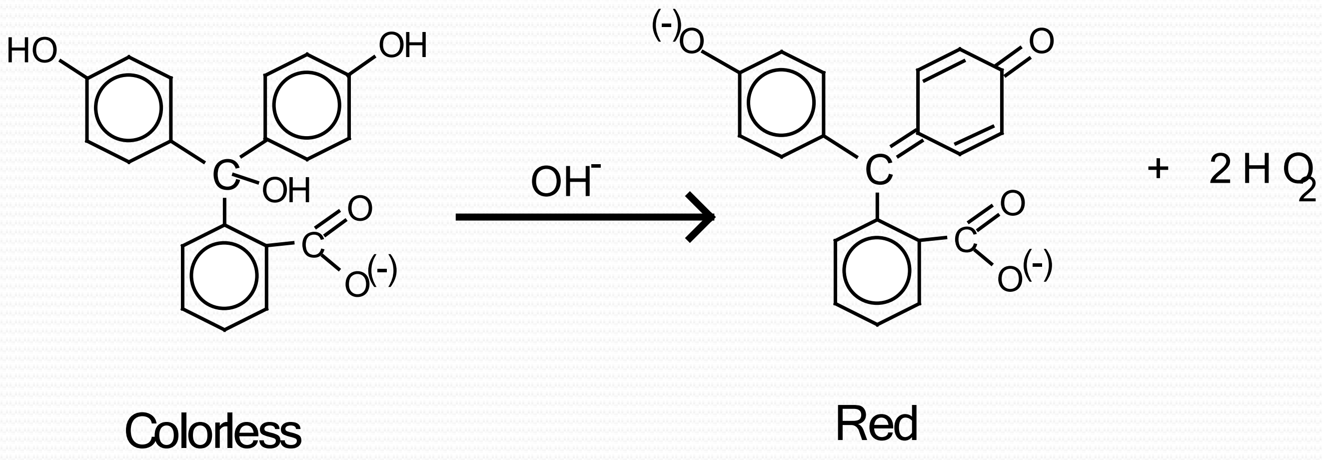


Yellow

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



Alkalinity procedures (cont.)

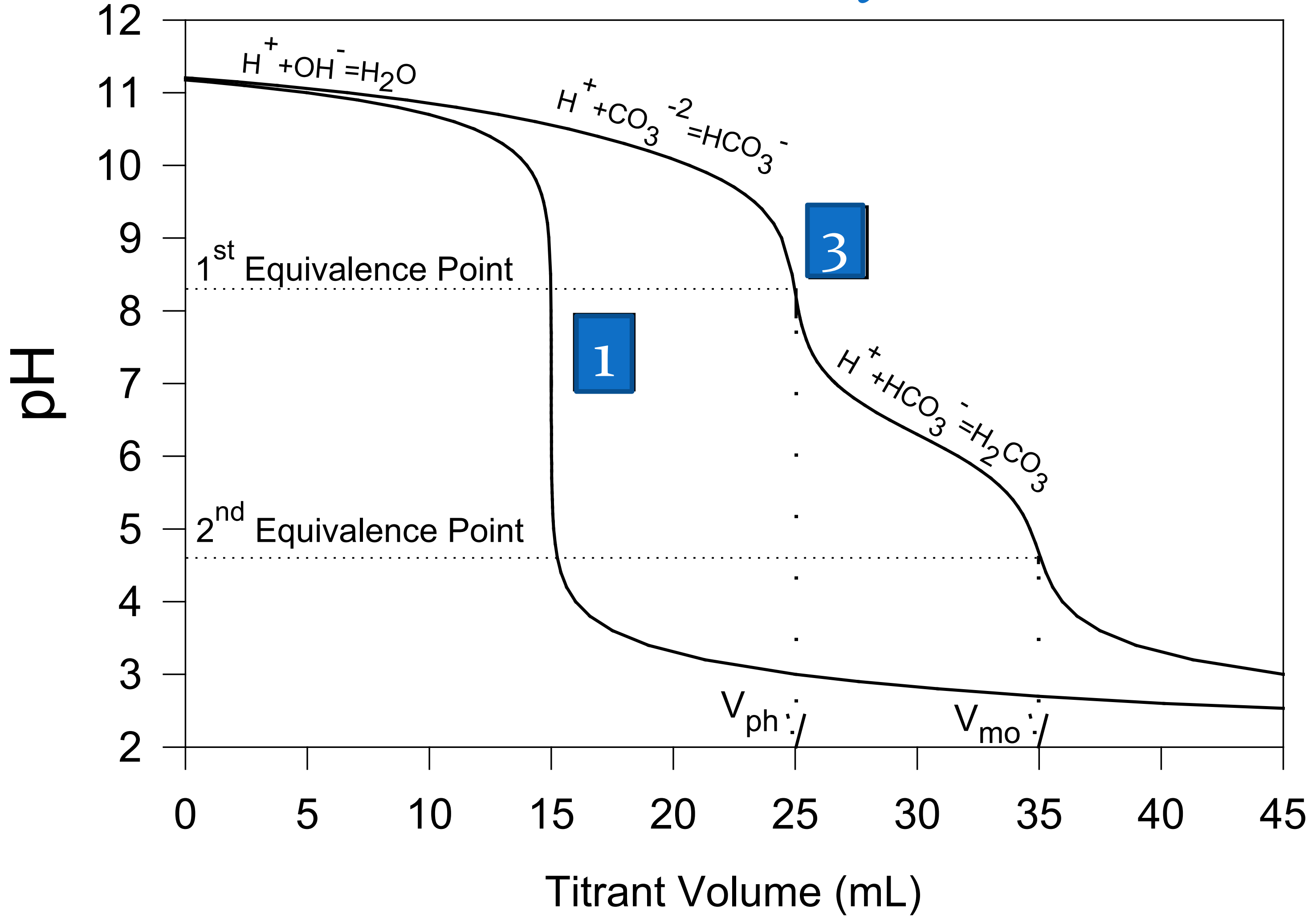
- calculations
  - $Equ_t = Equ_s$
  - $V_tN_t = V_sN_s$
  - $N_s = V_tN_t / V_s$
- Sliding endpoint depending on concentration

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 $CaCO_3$

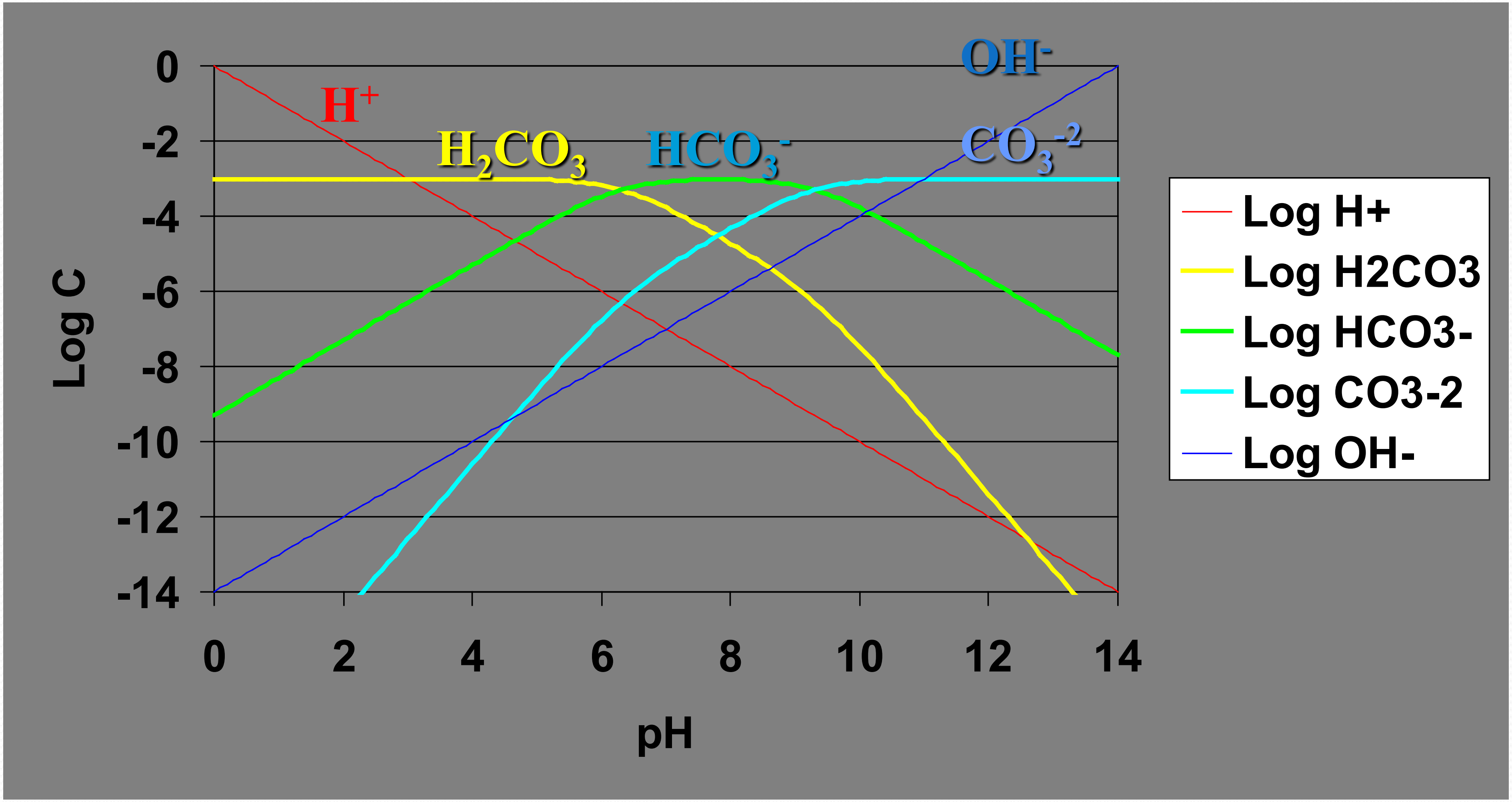
Types of Alkalinity

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

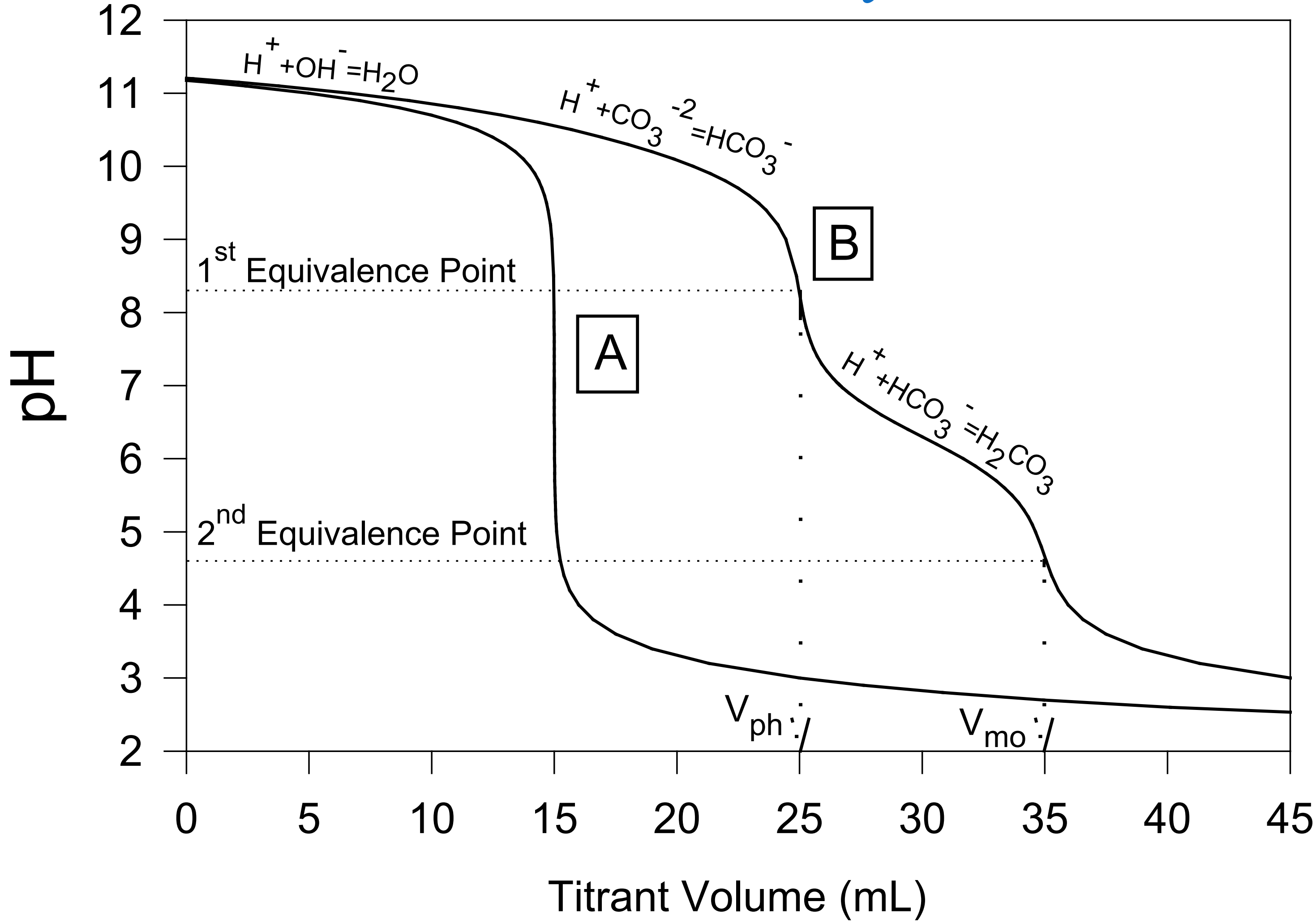
Scheme for Alk determination

- 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:
  - $Alk_{ph} = 50{,}000V_{ph}N_t/V_s$
  - $Alk_{mo} = 50{,}000V_{mo}N_t/V_s$

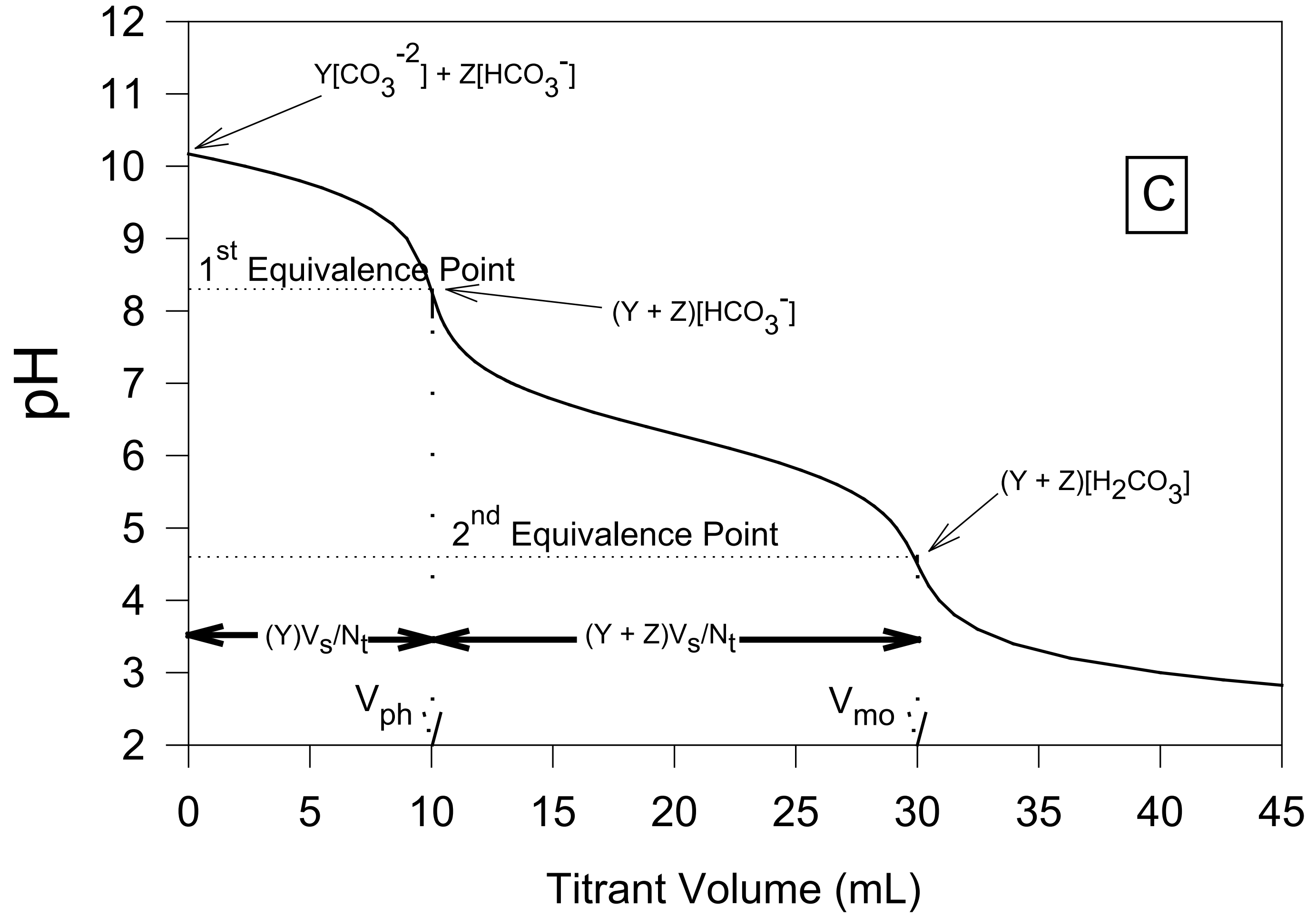
Carbonate System (C_T=10^{-3})



Acid Titration Curve for a Water Containing Hydroxide and Carbonate Alkalinity



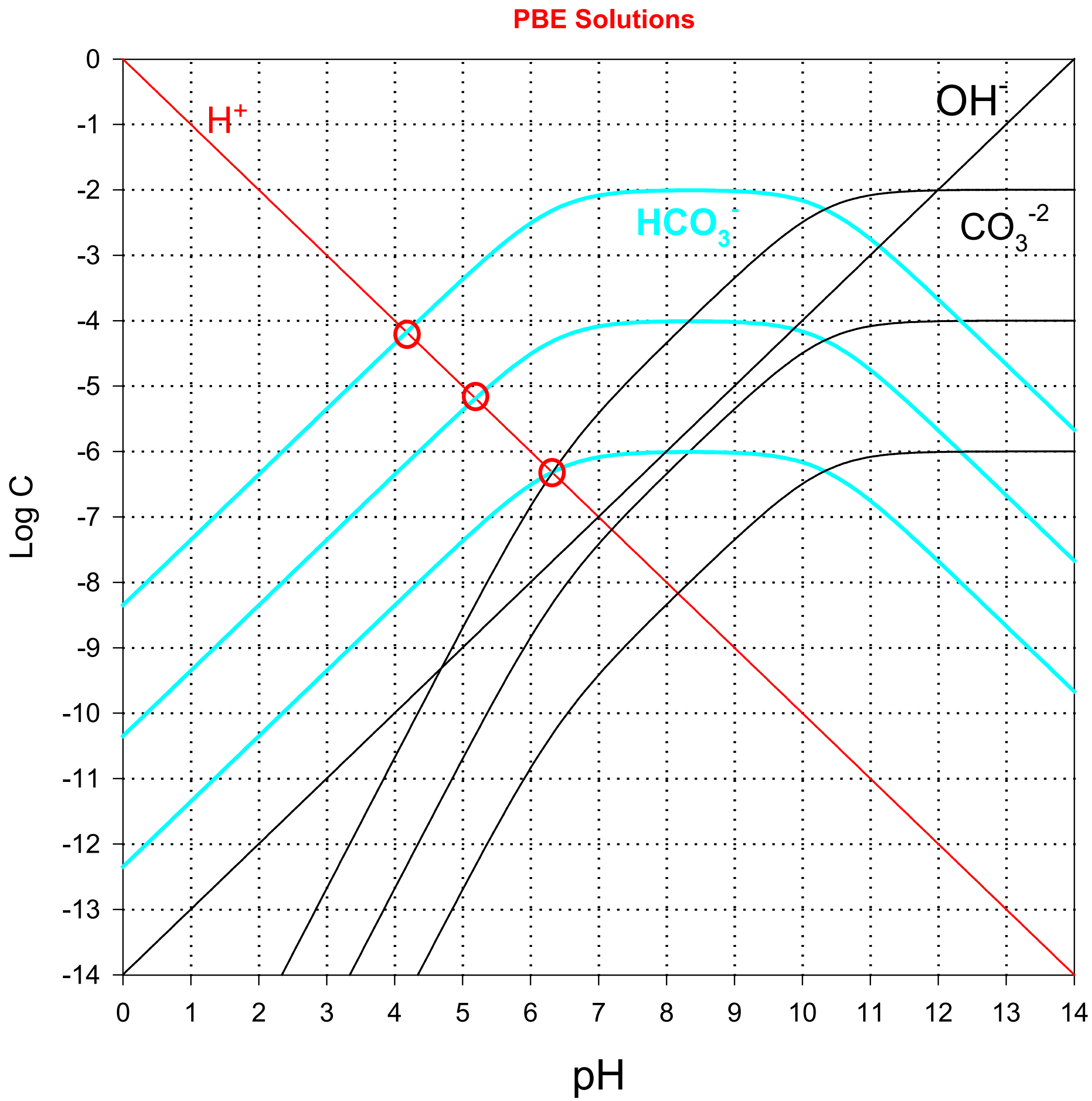
Acid Titration Curve for a Water Containing Carbonate and Bicarbonate Alkalinity



Alkalinity & titrations (cont.)

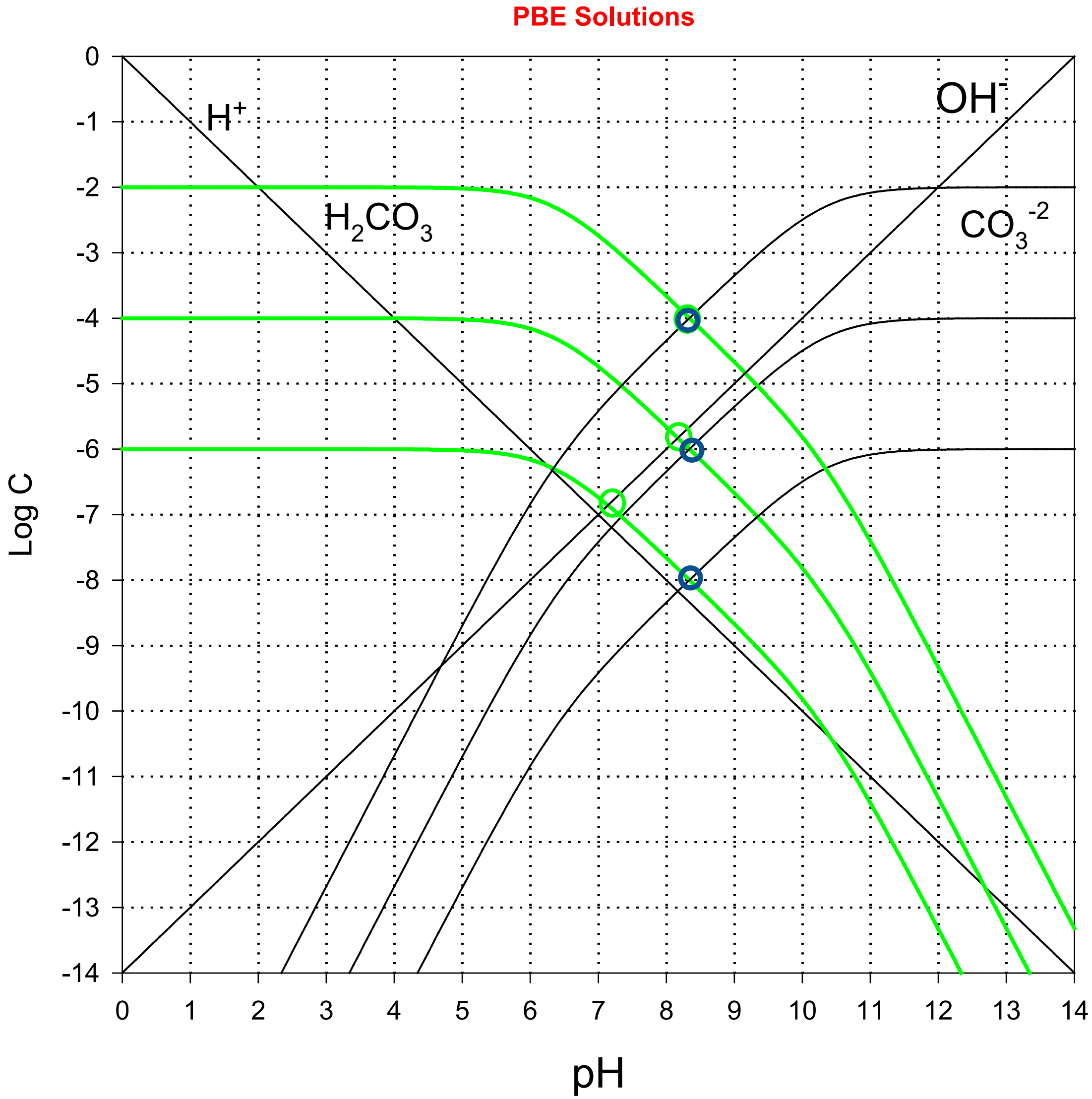
- Relationship between chemistry, titration and buffer intensity
  - See Stumm & Morgan, Figure 4.1 (pg. 154)
- Impact of C_T on titration endpoints
  - Refer to Benjamin, Figure 5.10
    - Also: Stumm & Morgan, Figure 4.3 (pg.157) and Pankow's Figure 9.2 (pg. 169)
- Conservation of Alkalinity
  - Stumm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

Pure H_2CO_3: f=0

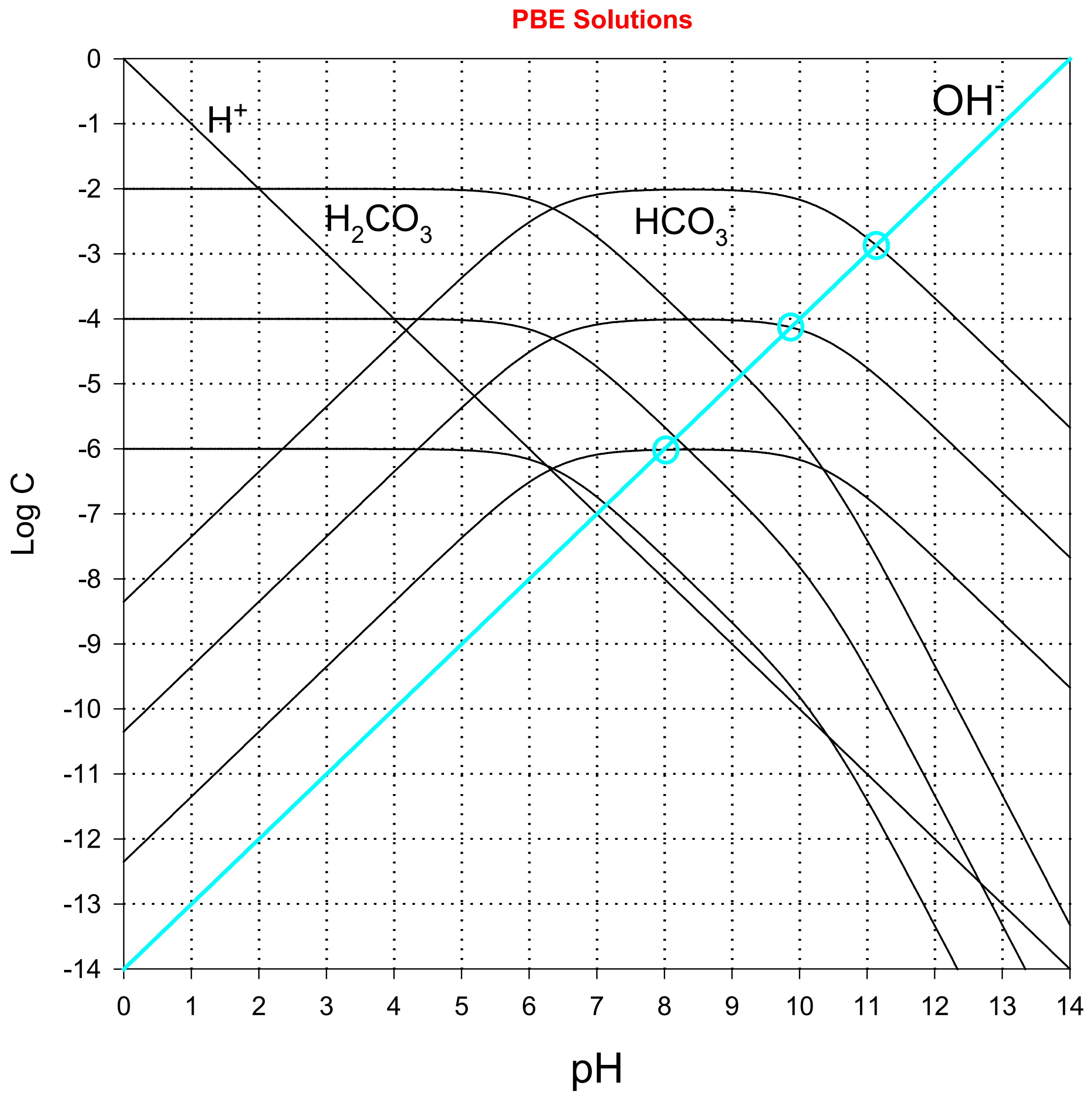


Pure HCO_3^-: f=1

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

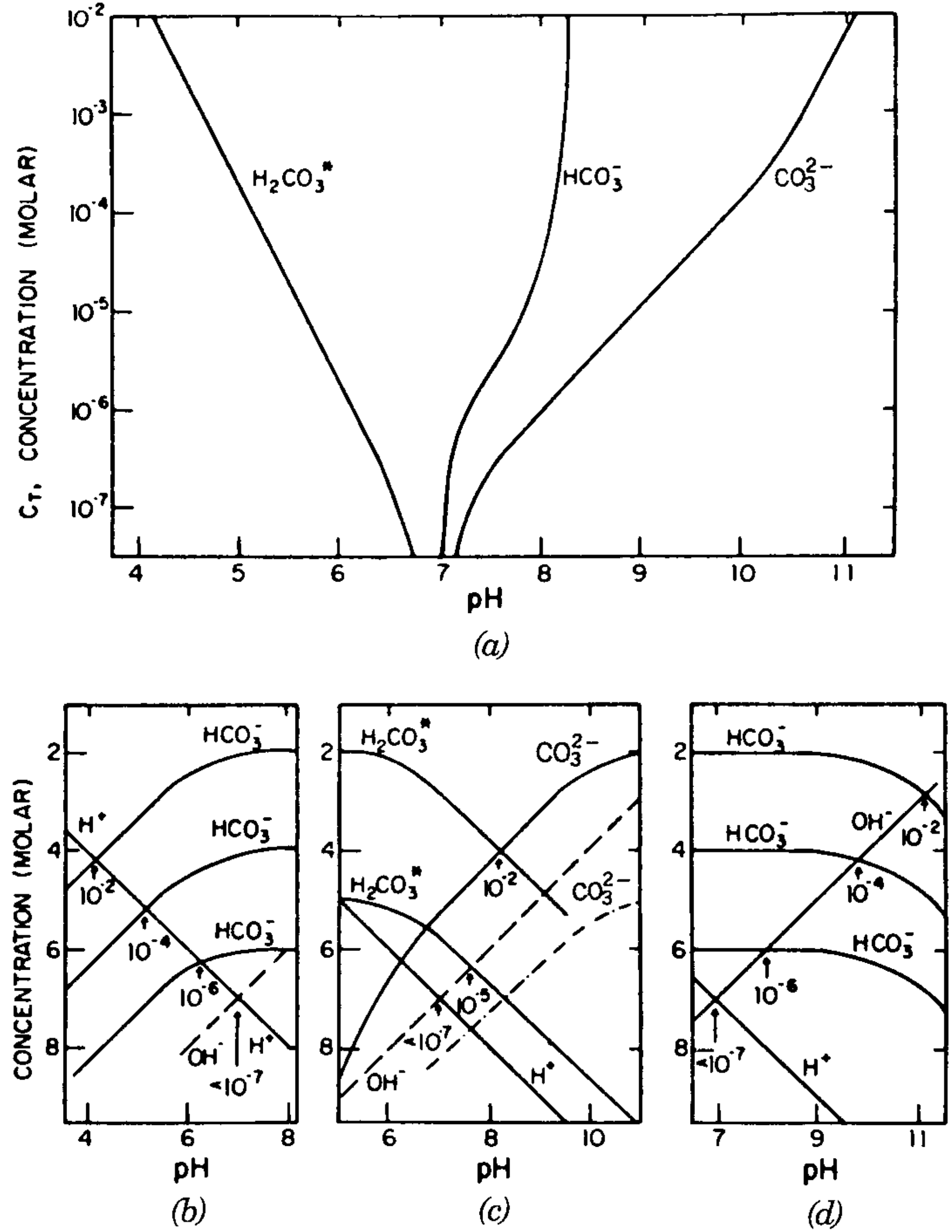


Pure CO_3^{-2}: f=2



PBE Solutions
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
Log C
H+
H2CO3
HCO3-
OH-
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH

Stumm & Morgan Figure 4.3; pg. 157



- To next lecture