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CEE 680: Water Chemistry

Lecture #23

Dissolved Carbon Dioxide: Open & Closed Systems IV

(Stumm & Morgan, Chapt.4)

Benjamin; Chapter 7

Conservation of Alk, C_T

- If you know any 2 of the following, you can calculate the 3rd
  - Alkalinity
  - pH
  - C_T or p_{CO_2}
- Conservative substances
  - Closed Systems
    - Alkalinity & C_T
  - Open Systems
    - Alkalinity

closed

$$Alk = (\alpha_1 + 2\alpha_2)C_T + [OH^-] - [H^+]$$

open

$$Alk = (\alpha_1 + 2\alpha_2)\frac{K_H p_{CO_2}}{\alpha_0} + [OH^-] - [H^+]$$

To solve these problems requires a **high level of precision** as Alk is often close in value to C_T, and the difference becomes very important

Alkalinity, C_T and pH

- Three types of problems are covered
  - Adding treatment chemicals to water
    - e.g., Soda Ash, Caustic, chlorine
  - Blending of waters
    - e.g., a surface water with a groundwater
  - Impacts of "internal" processes
    - The photosynthesis problem
- In each we ask about the final pH, Alkalinity and sometimes the C_T or carbonate species

Addition of Treatment Chemicals

Water	pH	C_T (mM)	Alk (meq/L)	Acy (meq/L)
"A"	6.5	1.7	1	2.4
A+ 0.7mM NaOH	8.3	1.7	1.7	1.7
A + 0.7mM Na_2CO_3	8.3	2.4	2.4	2.4

Assumes a closed system; now determine the composition of each in an open system; Also recall: $Alk_{tot} + Acy_{tot} = 2C_T$

Chlorine problem

- Starting water (B)
  - pH=8, Alkalinity = 82.5 mg-$CaCO_3$/L, NH_3-N=3.5 mg/L
    - Alk=1.65 meq/L, NH_3-N=0.25 mM
- Use breakpoint chlorination to remove ammonia-N (C)
  - $2NH_3 + 3Cl_2 = N_2(g) + 6H^+ + 6\ Cl^-$
- How much $NaHCO_3$ and NaOH must be added to reach pH 9.0 and 2.0 mM C_T? (D → E)

Snoeyink & Jenkins, example 4-39, pg.188

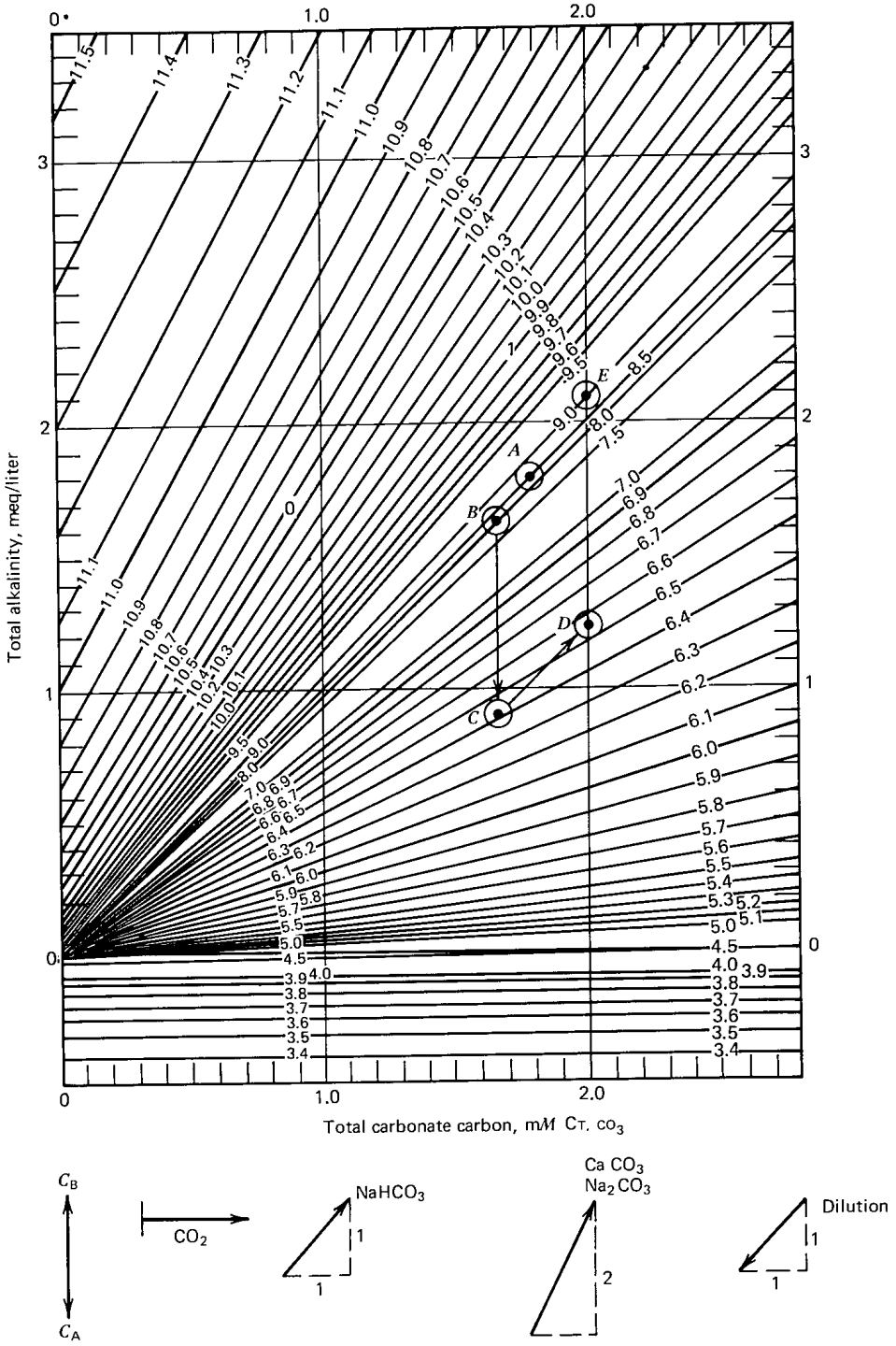
Deffeyes Diagram

$$Alk = (\alpha_1 + 2\alpha_2)C_T + [OH^-] - [H^+]$$

- For 15°C, closed system (has C_T, not p_{CO_2})
  - Snoeyink & Jenkins, pg187
  - Stumm & Morgan, pg 177
- Answer to previous problem
  - 0.35 mM $NaHCO_3$
  - 0.75 mM NaOH

D

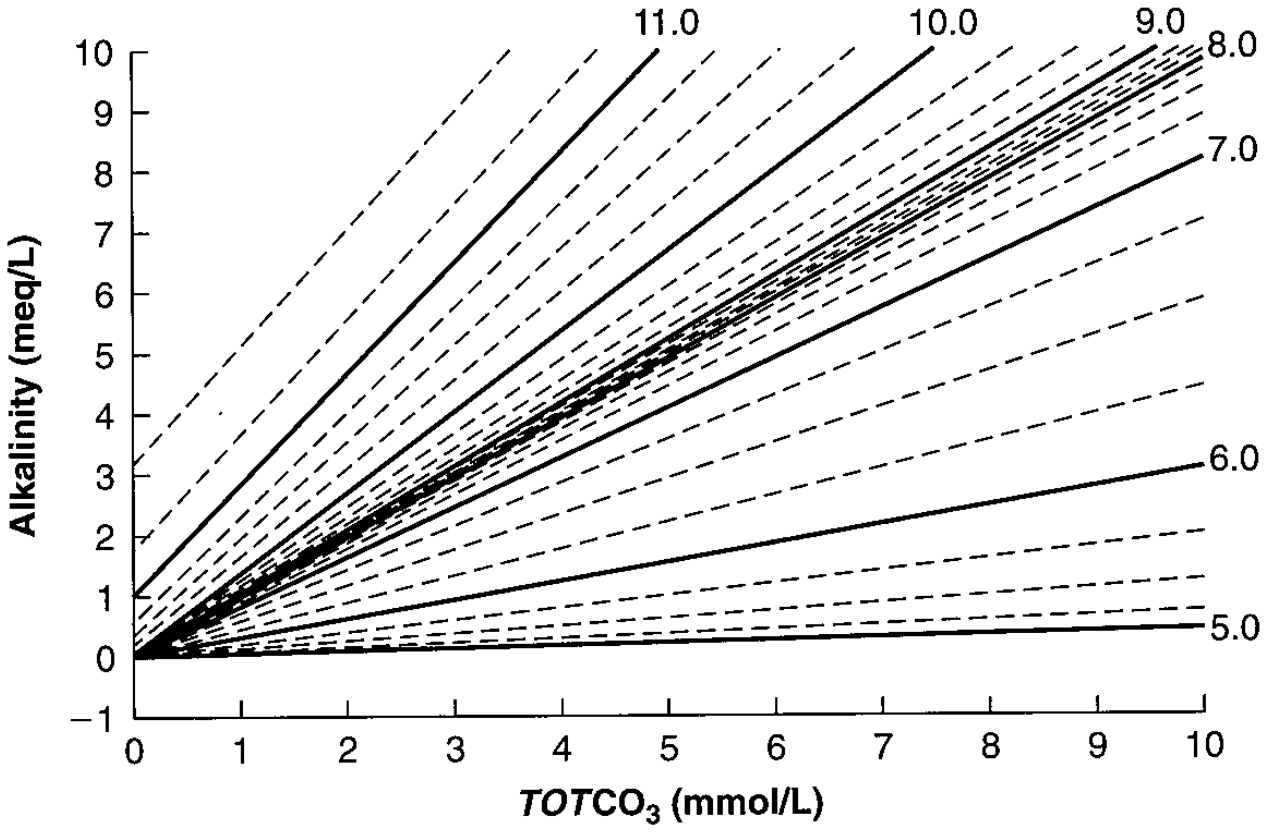
E



Ken Deffeyes
Princeton

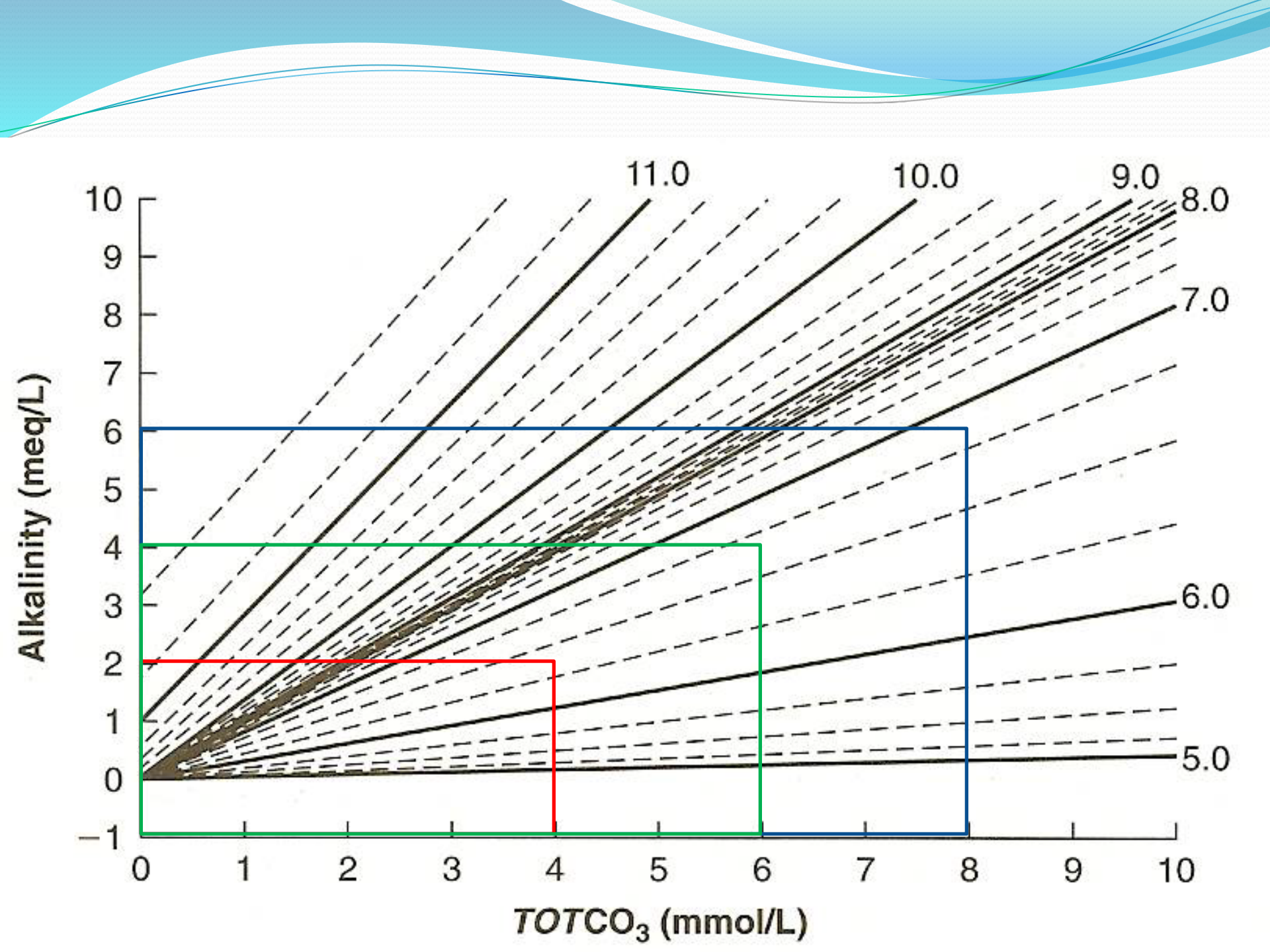
Nomograph

- Redrawn Deffeyes diagram
  - From Benjamin, 2002
    - Pg. 275



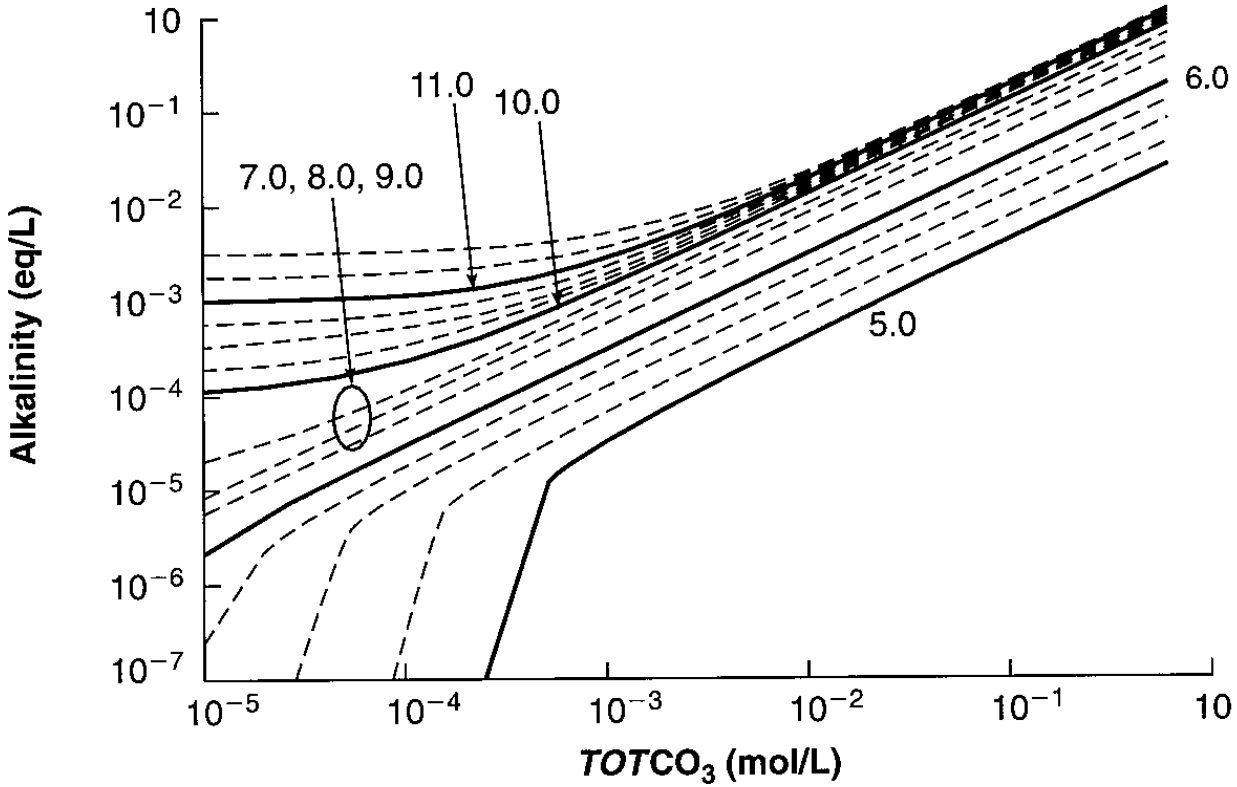
Blending of Waters

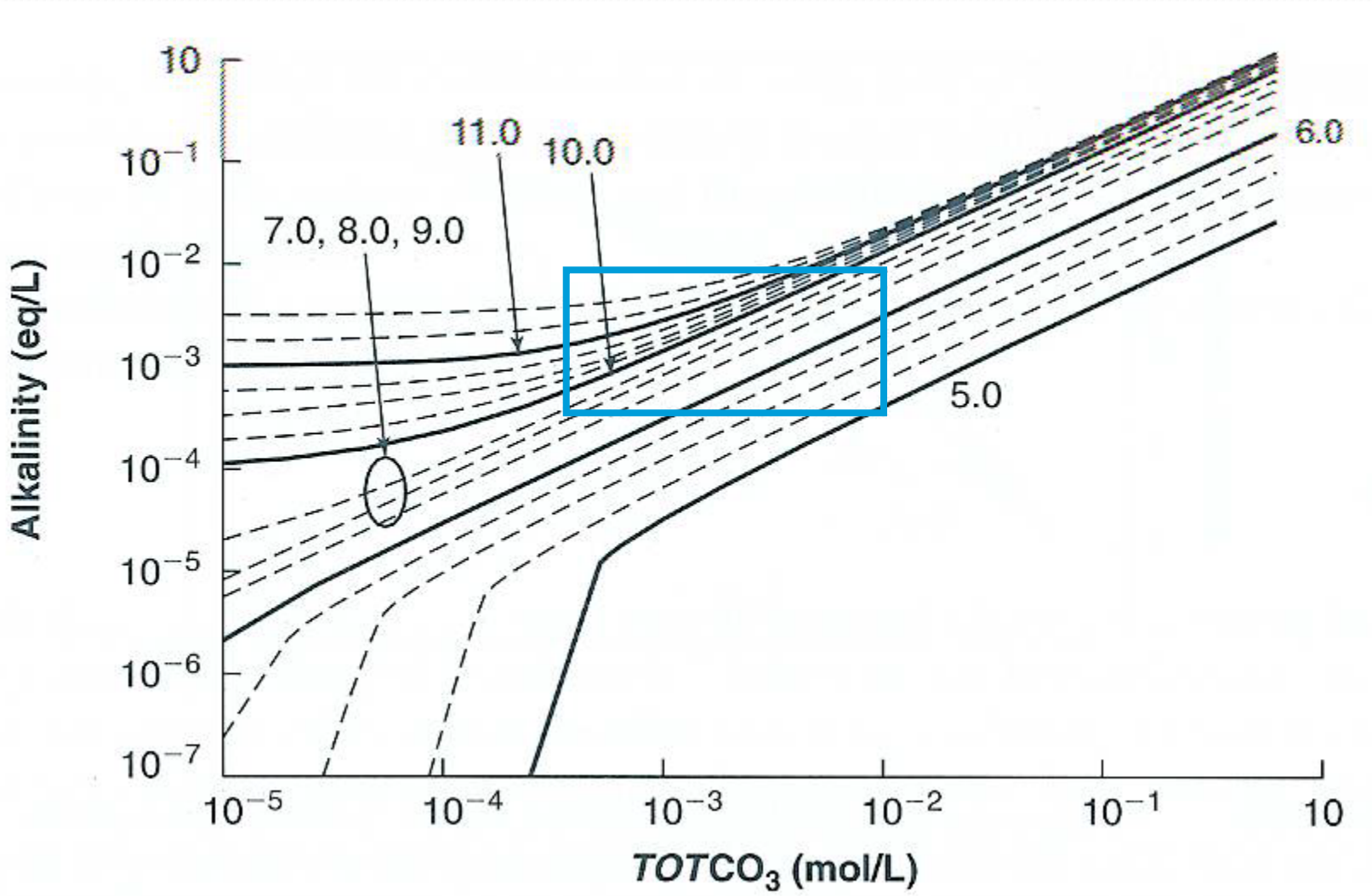
- Water A
  - C_T = 8 mM
  - Alk = 300 mg/L
  - pH = ?
- Water B
  - C_T = 4 mM
  - Alk = 100 mg/L
  - pH ?
- 50/50 Blend


11.0
10.0
9.0
8.0
7.0
6.0
5.0
Alkalinity (meq/L)
10
9
8
7
6
5
4
3
2
1
0
−1
0
1
2
3
4
5
6
7
8
9
10
TOTCO3 (mmol/L)

Nomograph

- Redrawn Deffeyes diagram
  - From Benjamin, 2002
    - Pg.275




Alkalinity (eq/L)
10
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
11.0
10.0
7.0, 8.0, 9.0
6.0
5.0
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10
$TOTCO_3$ (mol/L)

In-Class Practice

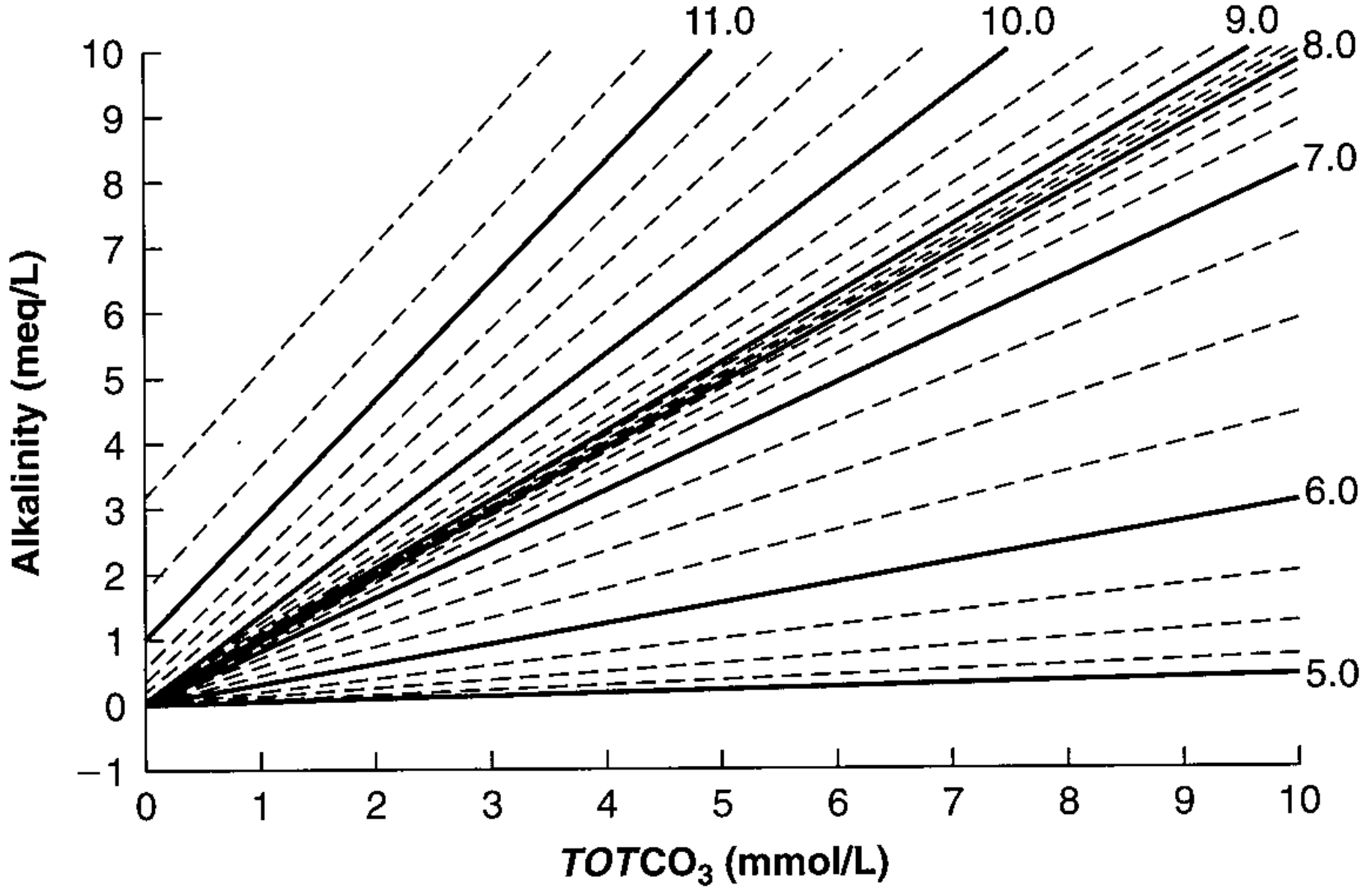
- For a closed system, what is the pH of:
  - 10^{-3} M solution of H_2CO_3
  - 10^{-3} M solution of $NaHCO_3$
  - 10^{-3} M solution of Na_2CO_3
- For an open system, what is the pH of:
  - 10^{-3} M solution of H_2CO_3
  - 10^{-3} M solution of $NaHCO_3$
  - 10^{-3} M solution of Na_2CO_3

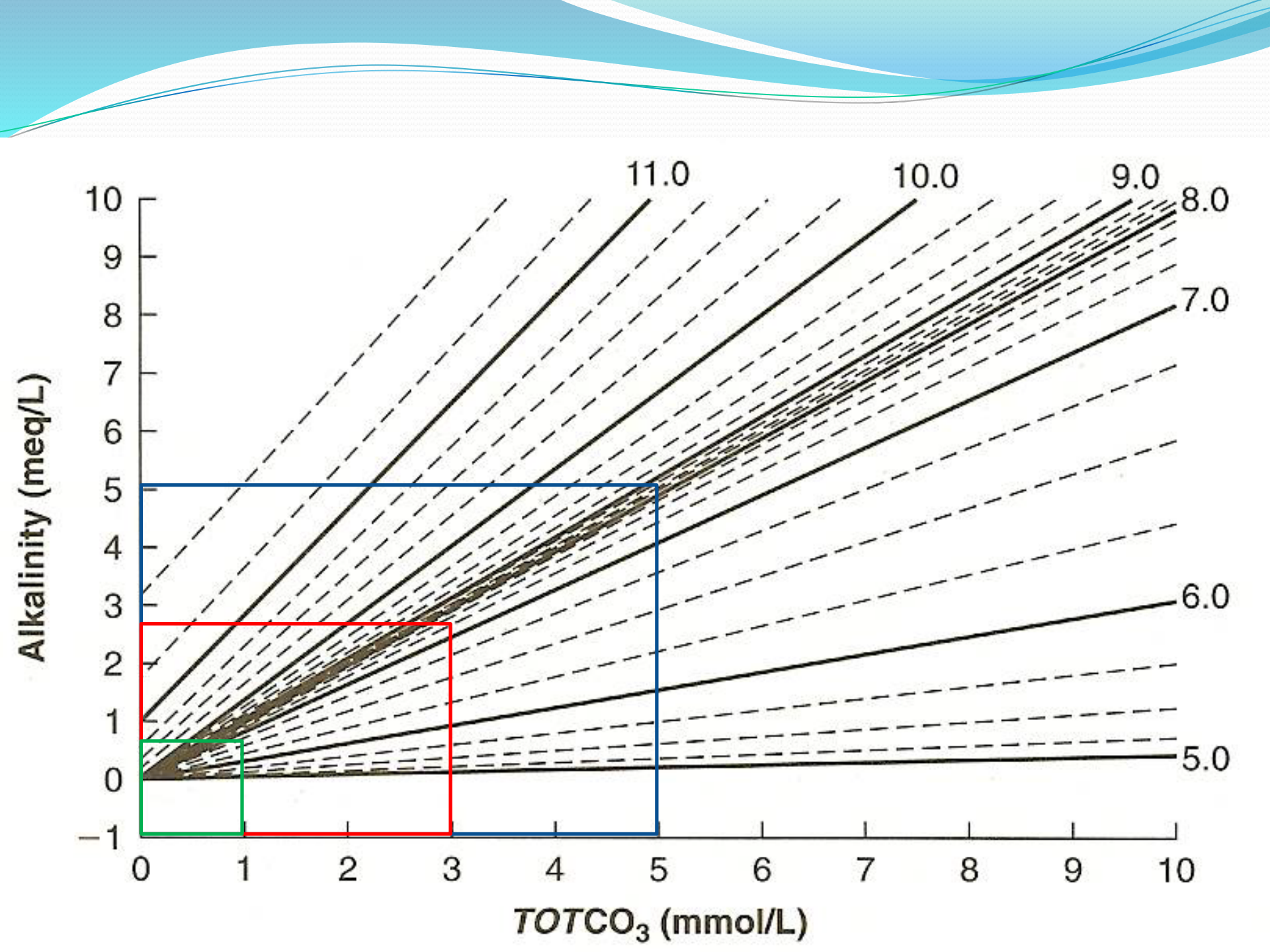
More practice

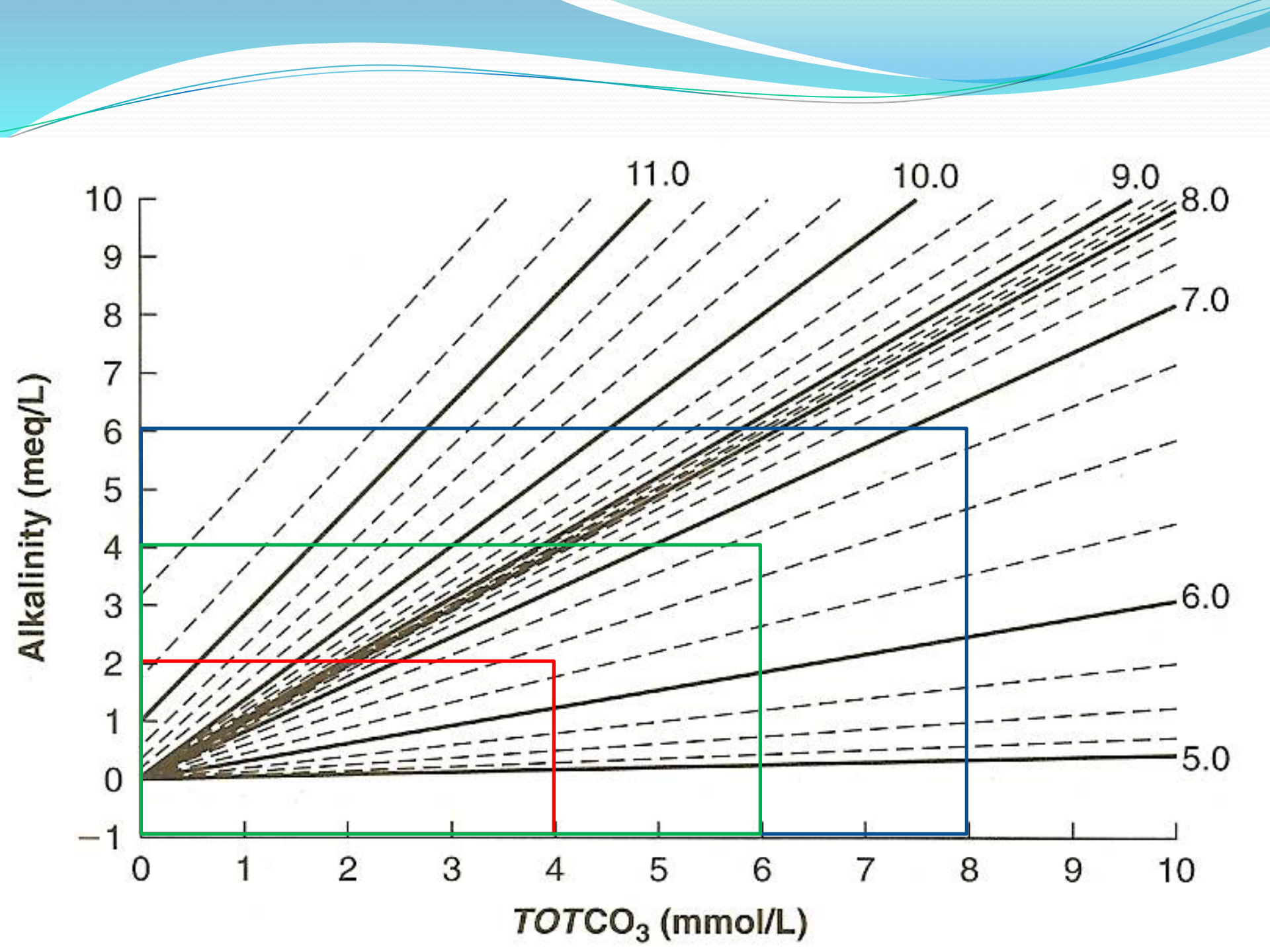
- What is the pH of a blend of the following:
  - 1 MGD of pH 6.5 water with a Alkalinity of 50 mg/L
  - 0.5 MGD of pH 8.5 water with an Alkalinity of 500 mg/L

$$Alk = (\alpha_1 + 2\alpha_2)\frac{K_H p_{CO_2}}{\alpha_0} + [OH^-] - [H^+]$$

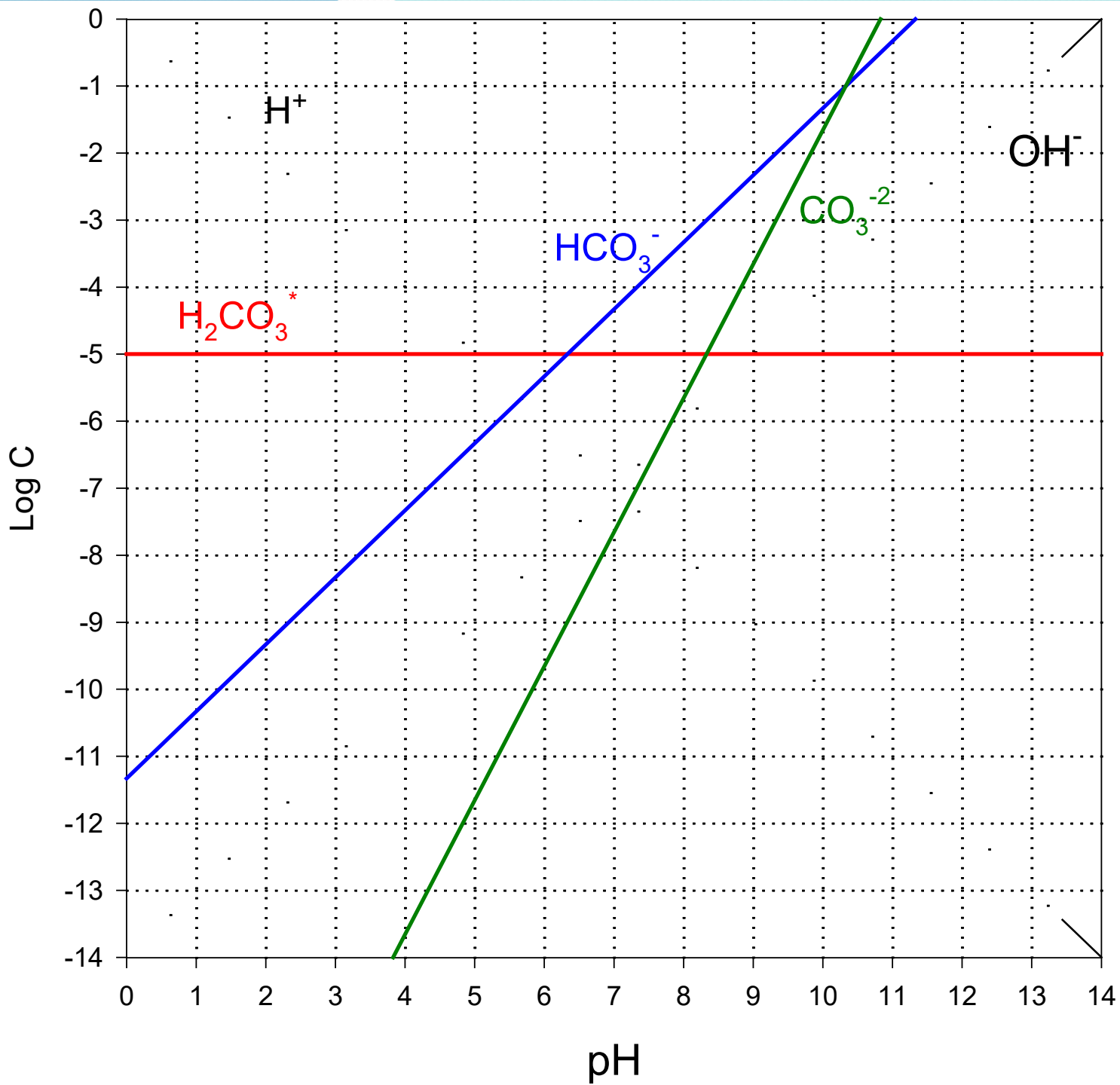
$$Alk = (\alpha_1 + 2\alpha_2)C_T + [OH^-] - [H^+]$$


11.0
10.0
9.0
8.0
7.0
6.0
5.0
Alkalinity (meq/L)
10
9
8
7
6
5
4
3
2
1
0
−1
0
1
2
3
4
5
6
7
8
9
10
TOTCO3 (mmol/L)


11.0
10.0
9.0
8.0
7.0
6.0
5.0
10
9
8
7
6
5
4
3
2
1
0
−1
0
1
2
3
4
5
6
7
8
9
10
Alkalinity (meq/L)
TOTCO3 (mmol/L)


11.0
10.0
9.0
8.0
7.0
6.0
5.0
Alkalinity (meq/L)
10
9
8
7
6
5
4
3
2
1
0
−1
0
1
2
3
4
5
6
7
8
9
10
TOTCO3 (mmol/L)

Open



David Reckhow

- To next lecture