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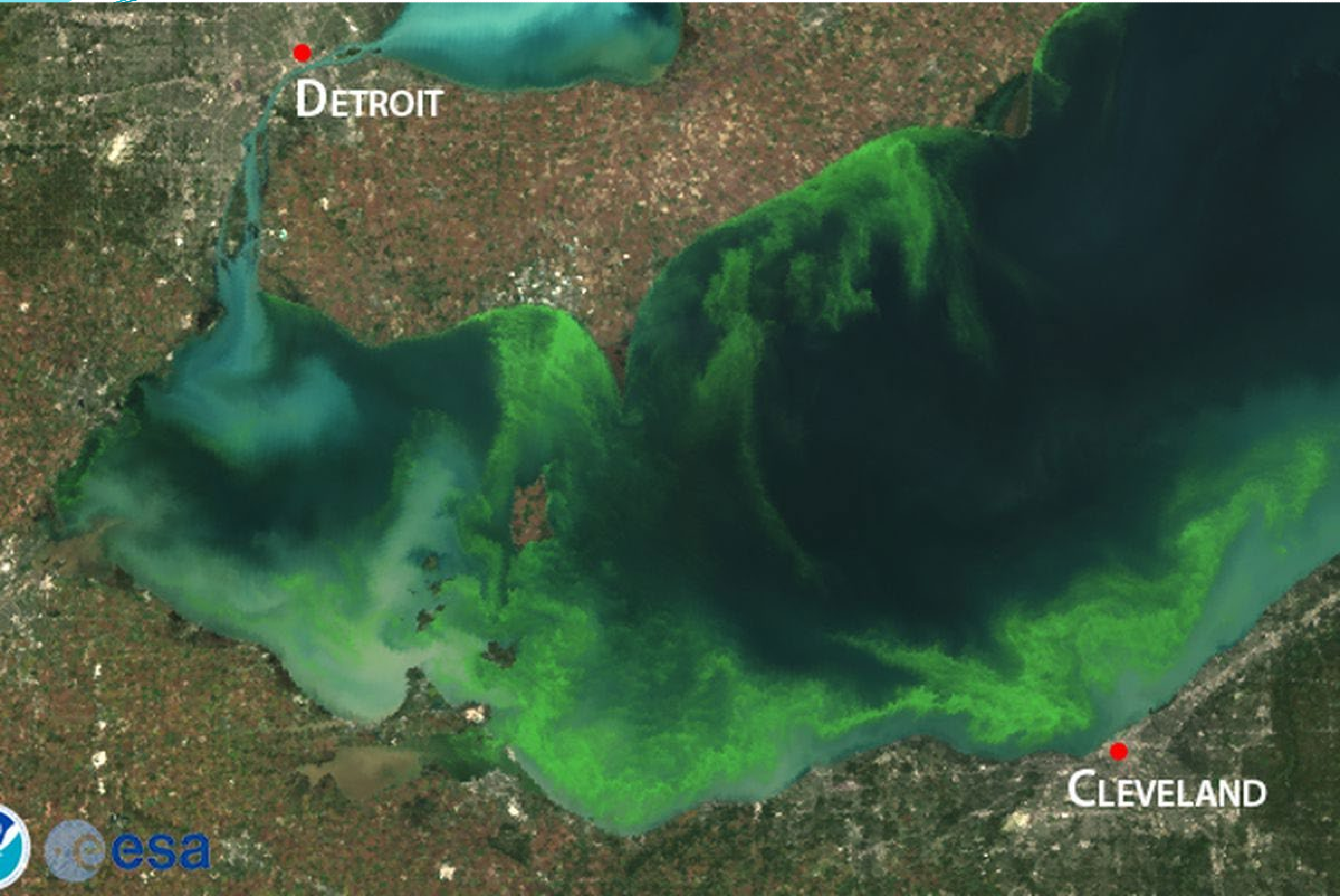
CEE 680: Water Chemistry

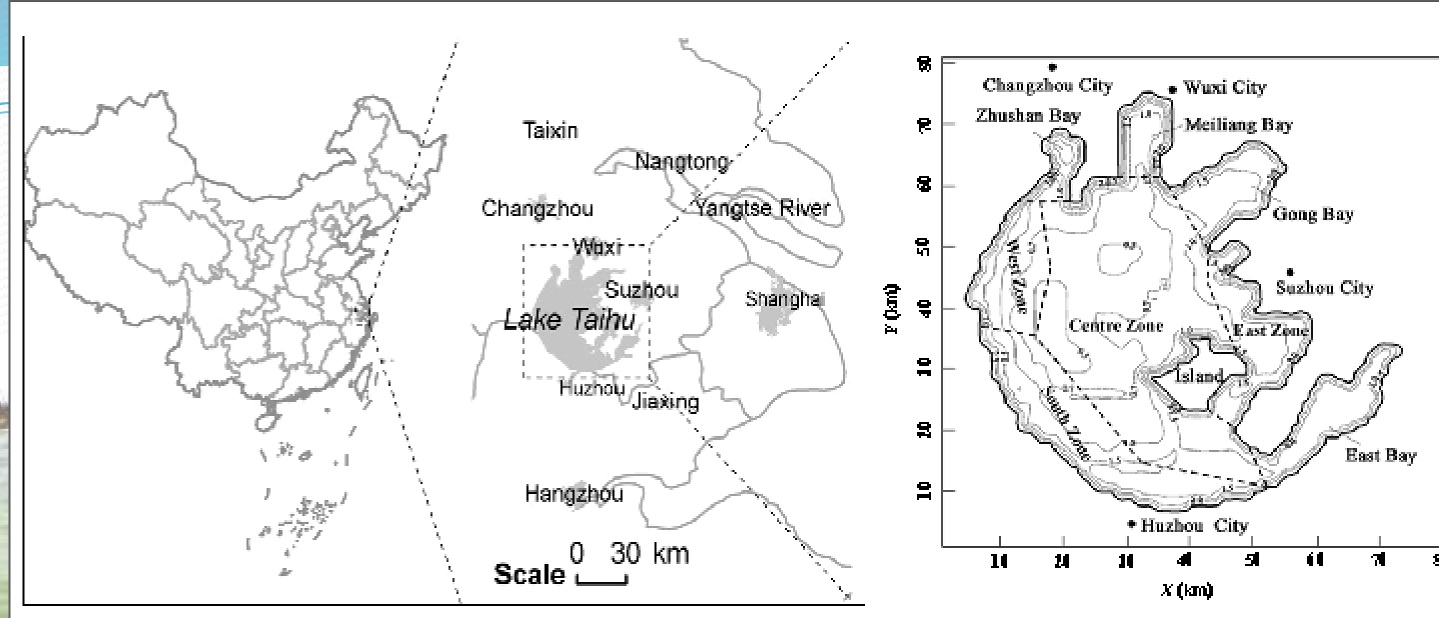
Lecture #25

Dissolved Carbon Dioxide: Open & Closed Systems VI

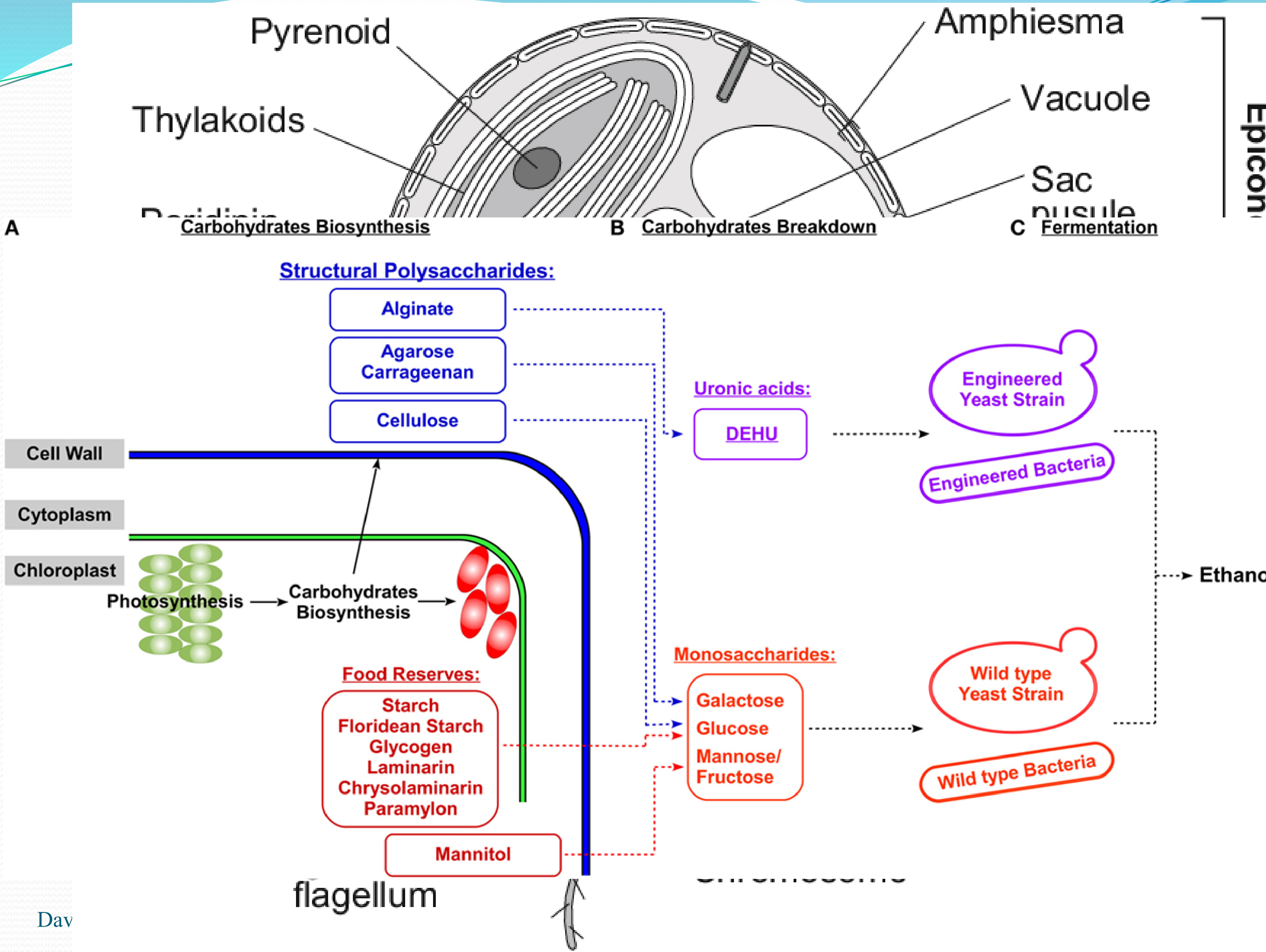
(Stumm & Morgan, Chapt.4)

Benjamin; Chapter 7


DETROIT
CLEVELAND
esa



Taixin
Nangtong
Changzhou
Yangtse River
Wuxi
Suzhou
Shangha
Lake Taihu
Huzhou
Jiaxing
Hangzhou
Scale
0 30 km
Changzhou City
Wuxi City
Zhushan Bay
Meiliang Bay
Gong Bay
Suzhou City
West Zone
Centre Zone
East Zone
Island
South Zone
East Bay
Huzhou City
Y (km)
X (km)



Pyrenoid
Thylakoids
Amphiesma
Vacuole
Sac
A Carbohydrates Biosynthesis
B Carbohydrates Breakdown
C Fermentation
Structural Polysaccharides:
Alginate
Agarose
Carrageenan
Cellulose
Cell Wall
Cytoplasm
Chloroplast
Photosynthesis
Carbohydrates Biosynthesis
Food Reserves:
Starch
Floridean Starch
Glycogen
Laminarin
Chrysolaminarin
Paramylon
Mannitol
Uronic acids:
DEHU
Monosaccharides:
Galactose
Glucose
Mannose/
Fructose
Engineered Yeast Strain
Engineered Bacteria
Wild type Yeast Strain
Wild type Bacteria
Ethanol
flagellum

Photosynthesis Problem

- Principles of conservation of Alk and C_T
  - From Stumm & Morgan (example 4.8, pg. 174)
- Approach
  - General: assume that system is closed
  - Simplified: treat alkalinity as constant
  - Alternative: allow alkalinity to vary in accordance with reaction stoichiometry

Problem Statement

- Photosynthesis with nitrate assimilation
  - $106\ CO_2 + 16\ NO_3^- + HPO_4^{-2} + 122\ H_2O + 18\ H^+$
    $= \ C_{106}H_{263}O_{110}N_{16}P + 138\ O_2$
- Conditions
  - Initial
    - Alk = 0.85 meq/L
    - pH = 9.0
  - Final (3 hours later)
    - pH = 9.5
- What is the net rate of carbon fixation?

Simplified Solution: (const. alk.)

- Use standard alkalinity equation

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

- So initially:

$$C_T = \frac{Alk - [OH^-] + [H^+]}{\alpha_1 + 2\alpha_2}$$
$$= \frac{8.5x10^{-4} - 10^{-5} + 10^{-9}}{0.9523 + 2(0.0477)}$$
$$= 8.017x10^{-4}\,M$$

$$\alpha_1 = \frac{1}{\cancelto{0}{\frac{[H^+]}{K_1}} + 1 + \frac{K_2}{[H^+]}} \approx \frac{1}{1 + \frac{10^{-10.3}}{10^{-9}}} \approx 0.9523$$

$$\alpha_2 = \frac{1}{\cancelto{0}{\frac{[H^+]^2}{K_1K_2}} + \frac{[H^+]}{K_2} + 1} \approx \frac{1}{\frac{10^{-9}}{10^{-10.3}} + 1} \approx 0.0477$$

Simplified Solution: (const. alk.)

- And 3 hours later

$$C_T = \frac{Alk - [OH^-] + [H^+]}{\alpha_1 + 2\alpha_2}$$

$$= \frac{8.5x10^{-4} - 10^{-4.5} - 10^{-9.5}}{0.8632 + 2(0.1368)}$$

$$= 7.199x10^{-4} M$$

$$\alpha_1 = \frac{1}{\cancelto{0}{\frac{[H^+]}{K_1}} + 1 + \frac{K_2}{[H^+]}} \approx \frac{1}{1 + \frac{10^{-10.3}}{10^{-9.5}}} \approx 0.8632$$

$$\alpha_2 = \frac{1}{\cancelto{0}{\frac{[H^+]^2}{K_1 K_2}} + \frac{[H^+]}{K_2} + 1} \approx \frac{1}{\frac{10^{-9.5}}{10^{-10.3}} + 1} \approx 0.1368$$

- So the rate is:

$$\Delta C_T / \Delta t = \frac{8.017x10^{-4} M - 7.199x10^{-4} M}{3hr}$$

$$= 2.7x10^{-5} M / hr$$

Alternative Solution

- Allow alkalinity to vary in accordance with reaction stoichiometry
  - $106\ CO_2 + 16\ NO_3^- + HPO_4^{-2} + 122\ H_2O + 18\ H^+$
    $= \ C_{106}H_{263}O_{110}N_{16}P + 138\ O_2$

$$\boxed{Alk_f = Alk_i + \tfrac{18}{106}\,{}^{\Delta}C_T}$$

- Now, incorporating this into the final alkalinity value:

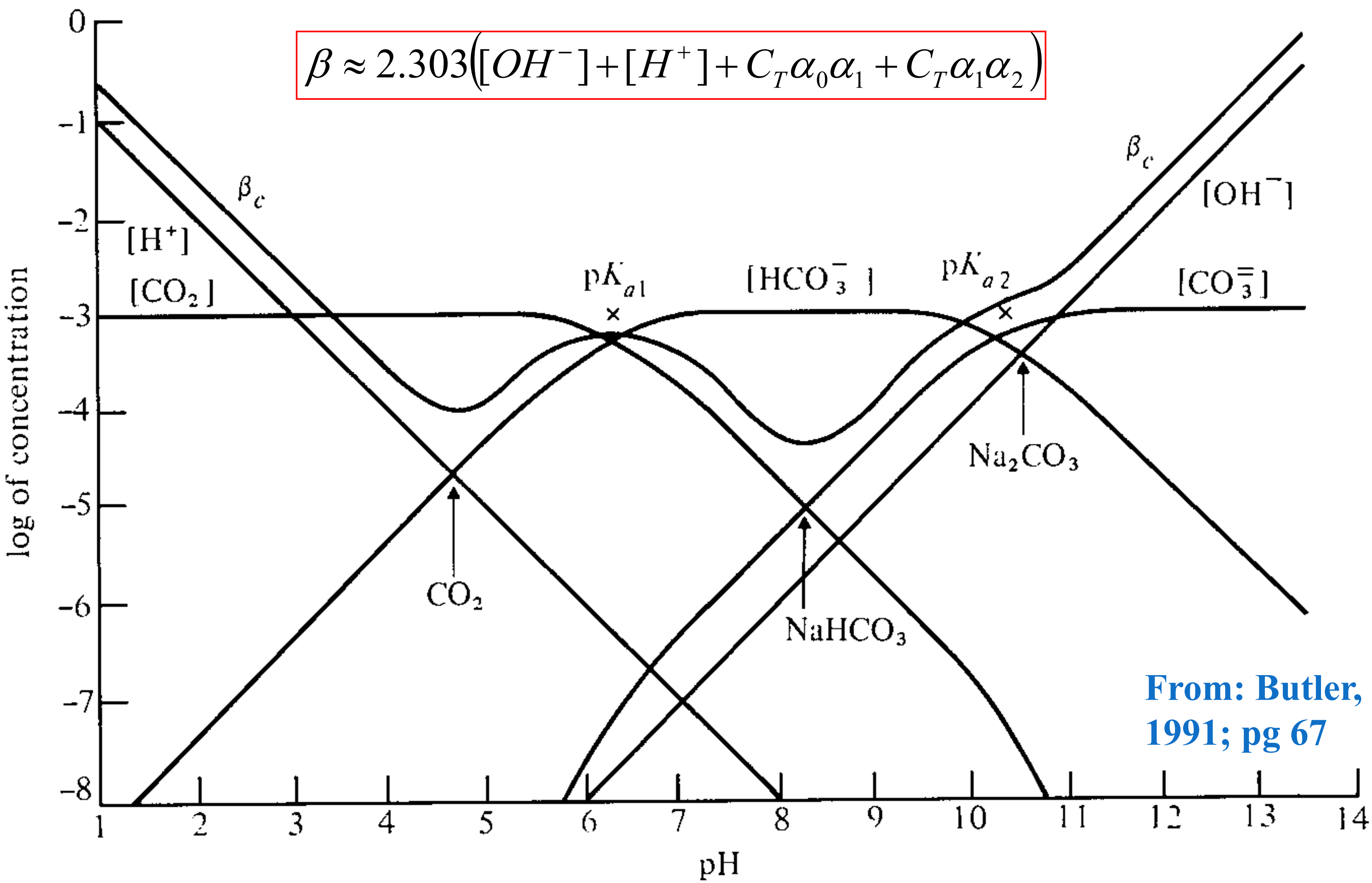
$$Alk = (\alpha_1 + 2\alpha_2)C_T + [OH^-] - [H^+]$$
$$Alk_f - [OH^-]_f = (\alpha_1 + 2\alpha_2)_f \left(C_{T_i} - {}^{\Delta}C_T\right)$$
$$8.5x10^{-4} + \tfrac{18}{106}\,{}^{\Delta}C_T - 10^{-4.5} = 1.136\left(8.017x10^{-4} - {}^{\Delta}C_T\right)$$
$$1.3066\,{}^{\Delta}C_T = 9.2995x10^{-5}$$
$${}^{\Delta}C_T = 7.1x10^{-5}$$

- And the rate becomes:

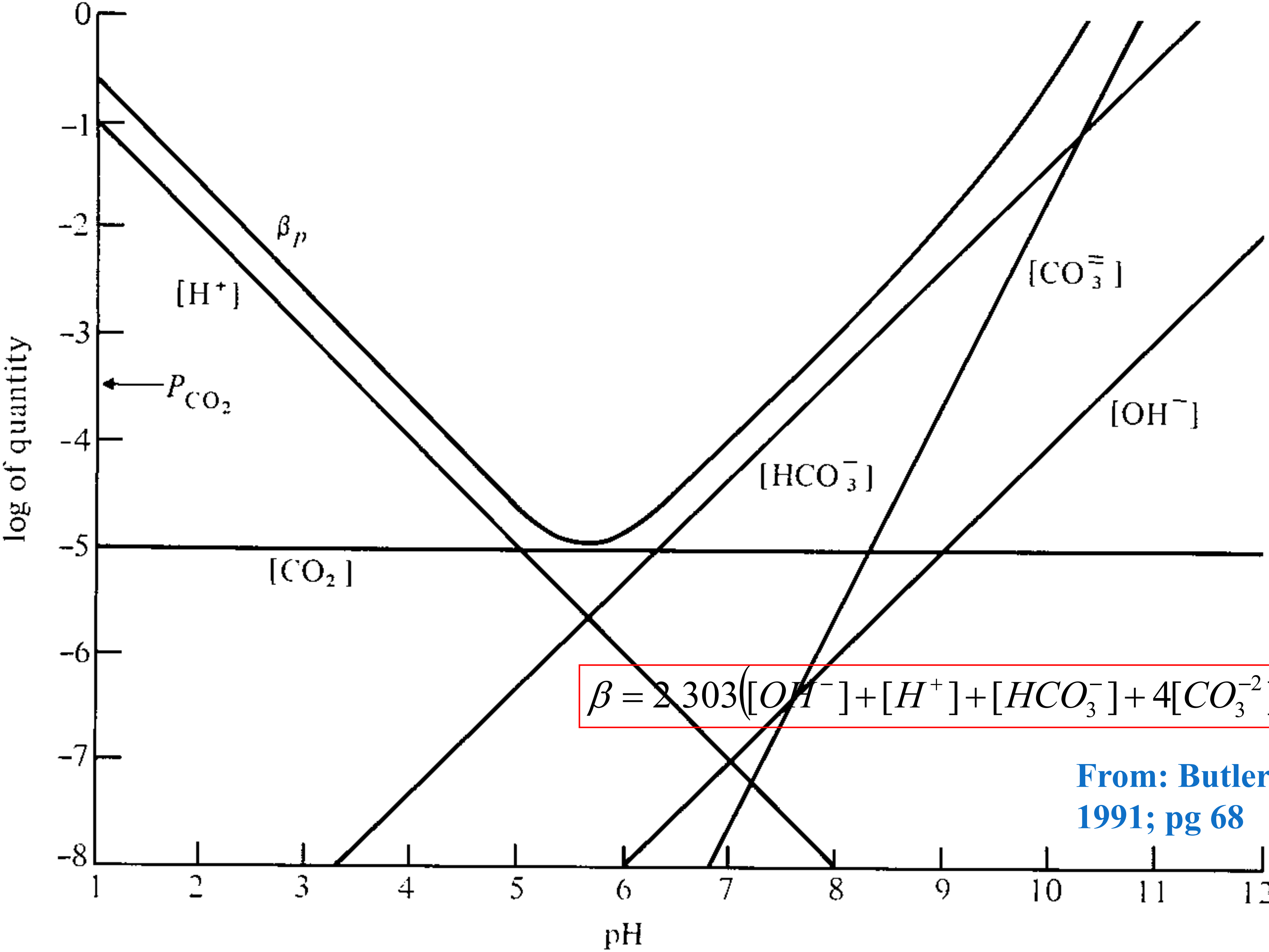
$${}^{\Delta}C_T \Big/ {}^{\Delta}t = \frac{7.1x10^{-5}M}{3hr} = 2.4x10^{-5} M/hr$$

Buffer Intensity & Closed System

$$\beta \approx 2.303\left([OH^-]+[H^+]+C_T\alpha_0\alpha_1+C_T\alpha_1\alpha_2\right)$$



From: Butler, 1991; pg 67



$$\boxed{\beta = 2.303\left([OH^-]+[H^+]+[HCO_3^-]+4[CO_3^{-2}]\right)}$$

From: Butler, 1991; pg 68

- To next lecture

DAR