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CEE 680: Water Chemistry

Lecture #40

Precipitation and Dissolution: Metal Carbonates & Hydroxides

(Stumm & Morgan, Chapt.7)

Benjamin; Chapter 8.7-8.15

Topics

- Ferrous Carbonate
  - vs C_T
- Mixed carbonate/hydroxide diagrams
  - Log C vs pH
  - Predominance diagrams

Siderite

- Ferrous Carbonate
  - Images from Wikipedia

Ferrous Carbonate/Hydroxide

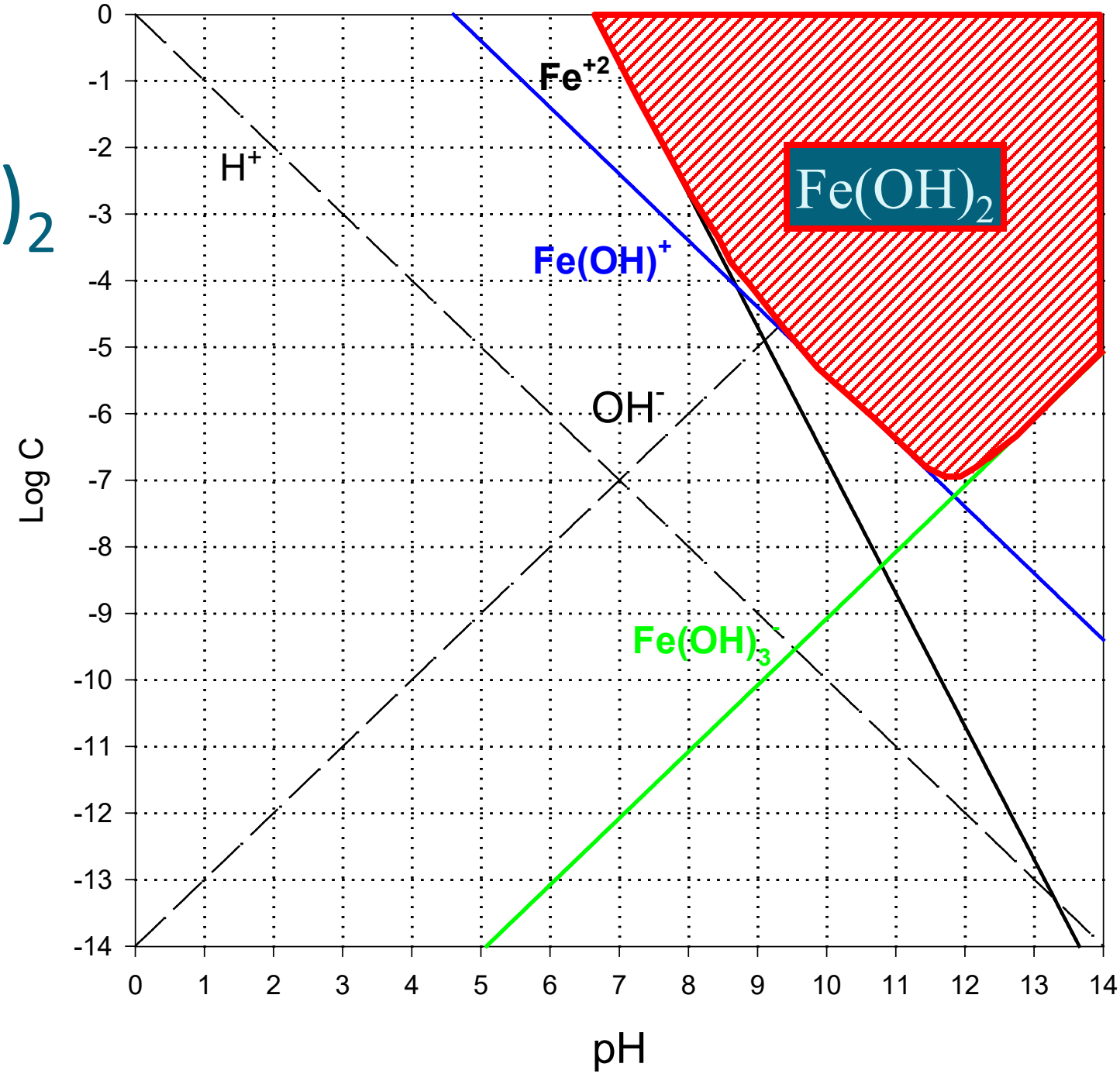
- Hydroxide Equilibria — **Log K**
  - $Fe(OH)_2(s) = Fe^{+2} + 2OH^-$ — -14.5
  - $Fe(OH)_2(s) = FeOH^+ + OH^-$ — -9.4
  - $Fe(OH)_2(s) + OH^- = Fe(OH)_3^-$ — -5.1
- Carbonate Equilibria
  - $FeCO_3(s) = Fe^{+2} + CO_3^{-2}$ — -10.7
  - $FeCO_3(s) + OH^- = FeOH^+ + CO_3^{-2}$ — -5.6
  - $FeCO_3(s) + 3OH^- = Fe(OH)_3^- + CO_3^{-2}$ — -1.3

$$\alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1}$$

Carbonate and hydroxide system

- We could graph the same soluble species in equilibrium with $FeCO_{3(s)}$ and plot it versus free log ligand concentration (eg., CO_3^{-2}).
  - This would look a lot like the ferrous hydroxide figure
  - It would not allow us to plot both against the same independent variable
    - It would not help us understand the relative competition between ferrous carbonate and ferrous hydroxide precipitation
- Instead we use a single independent variable (pH) so we can compare the two

$Fe(OH)_2$



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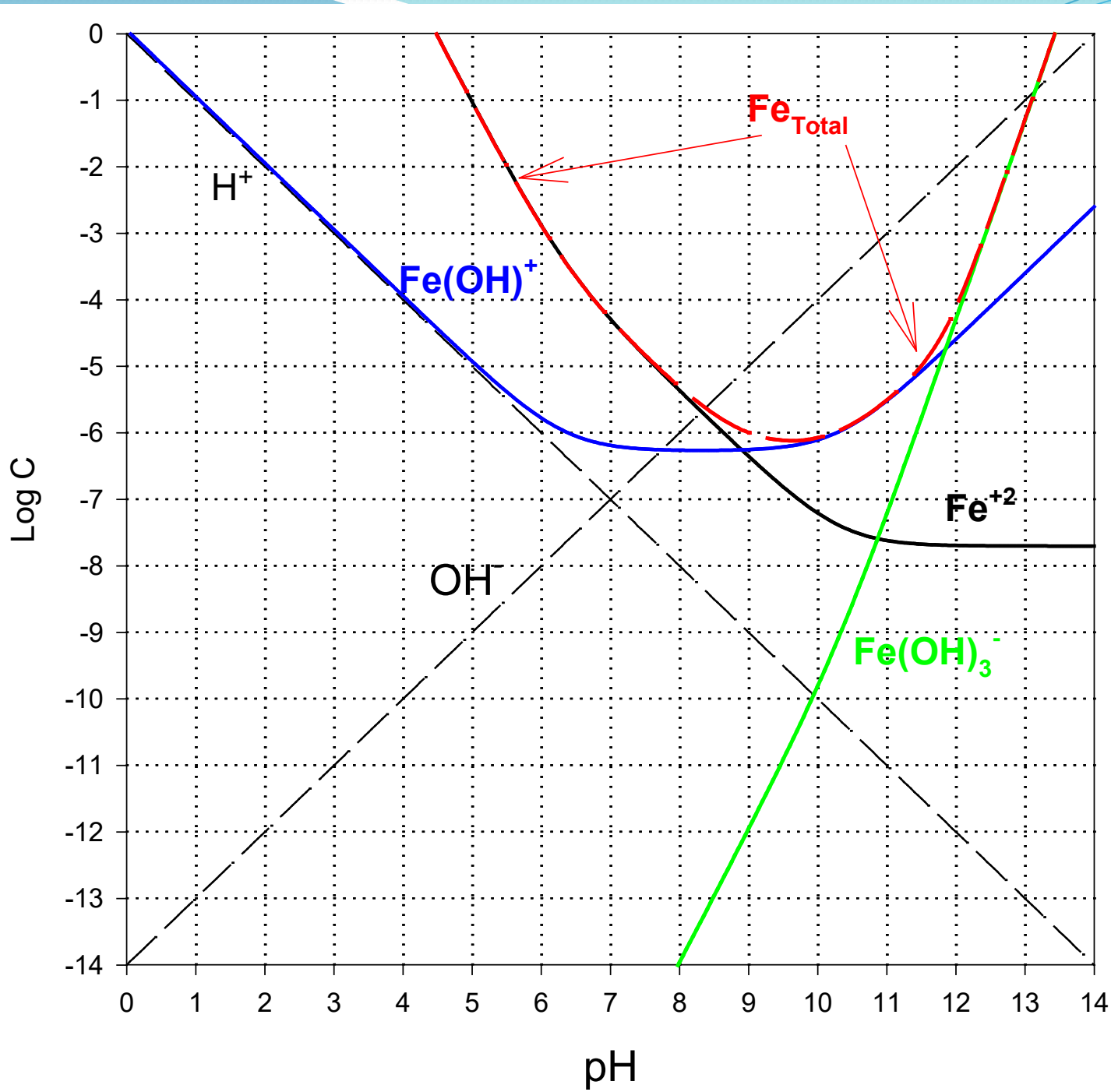
$FeCO_3$



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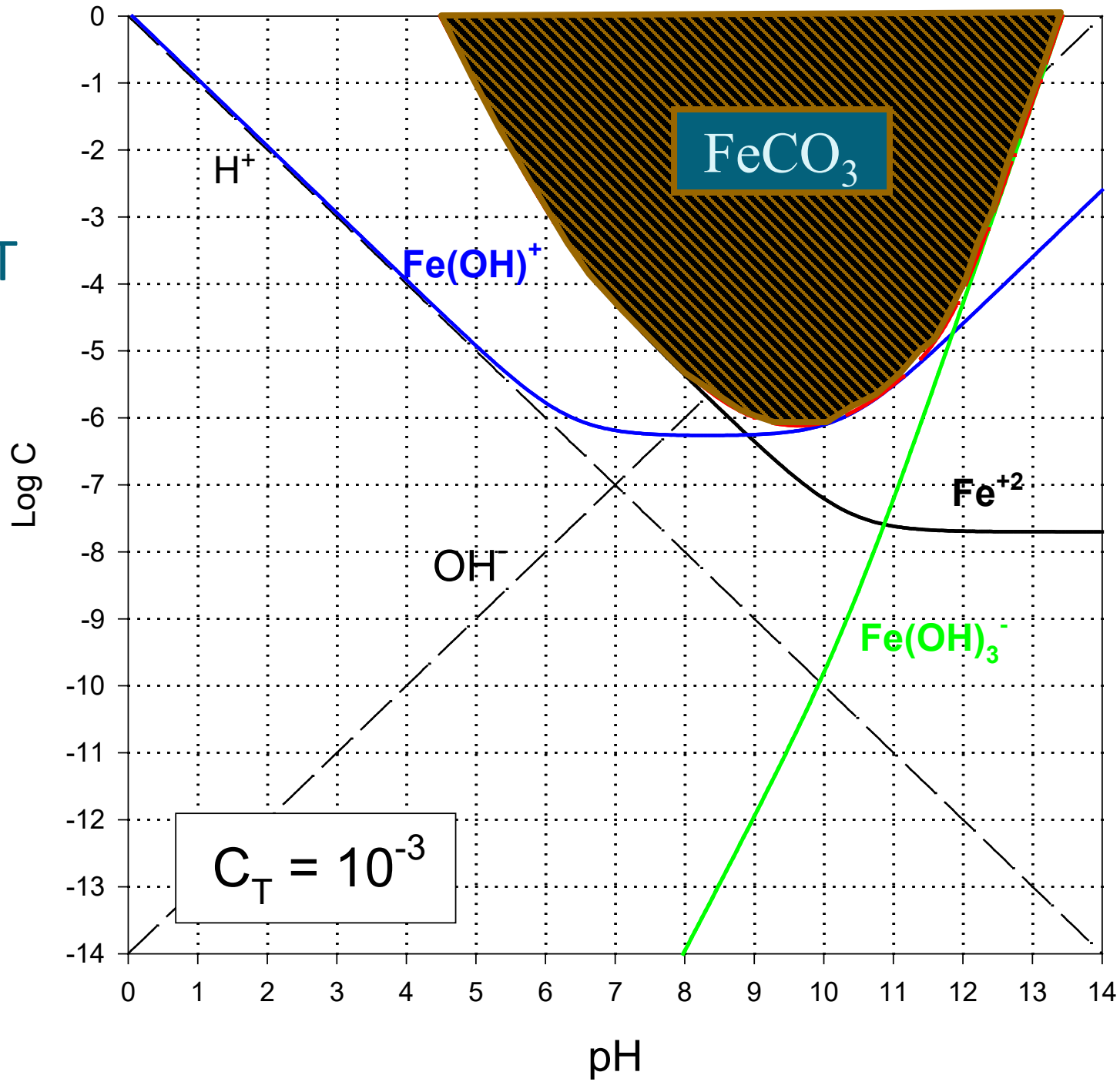
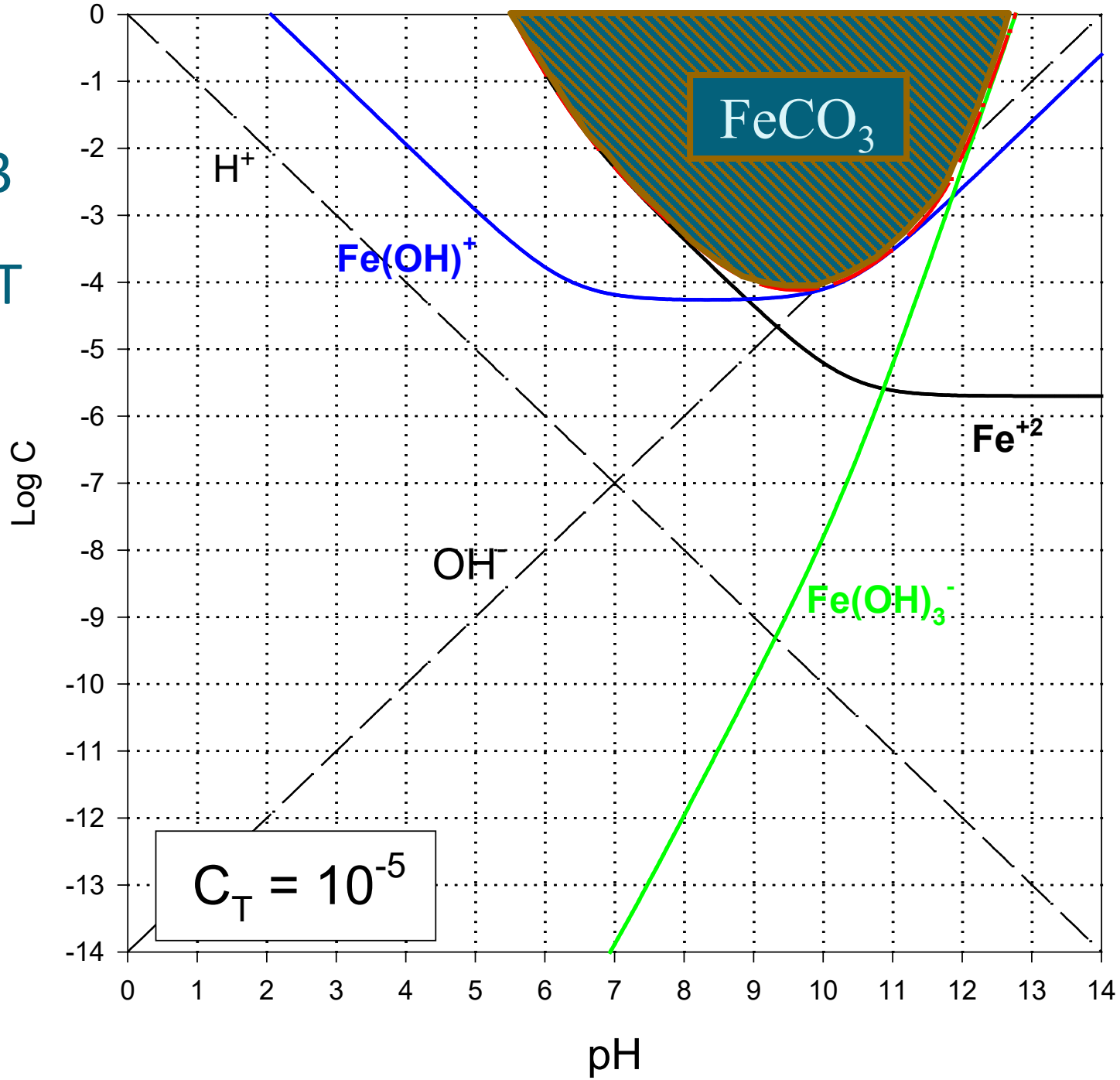
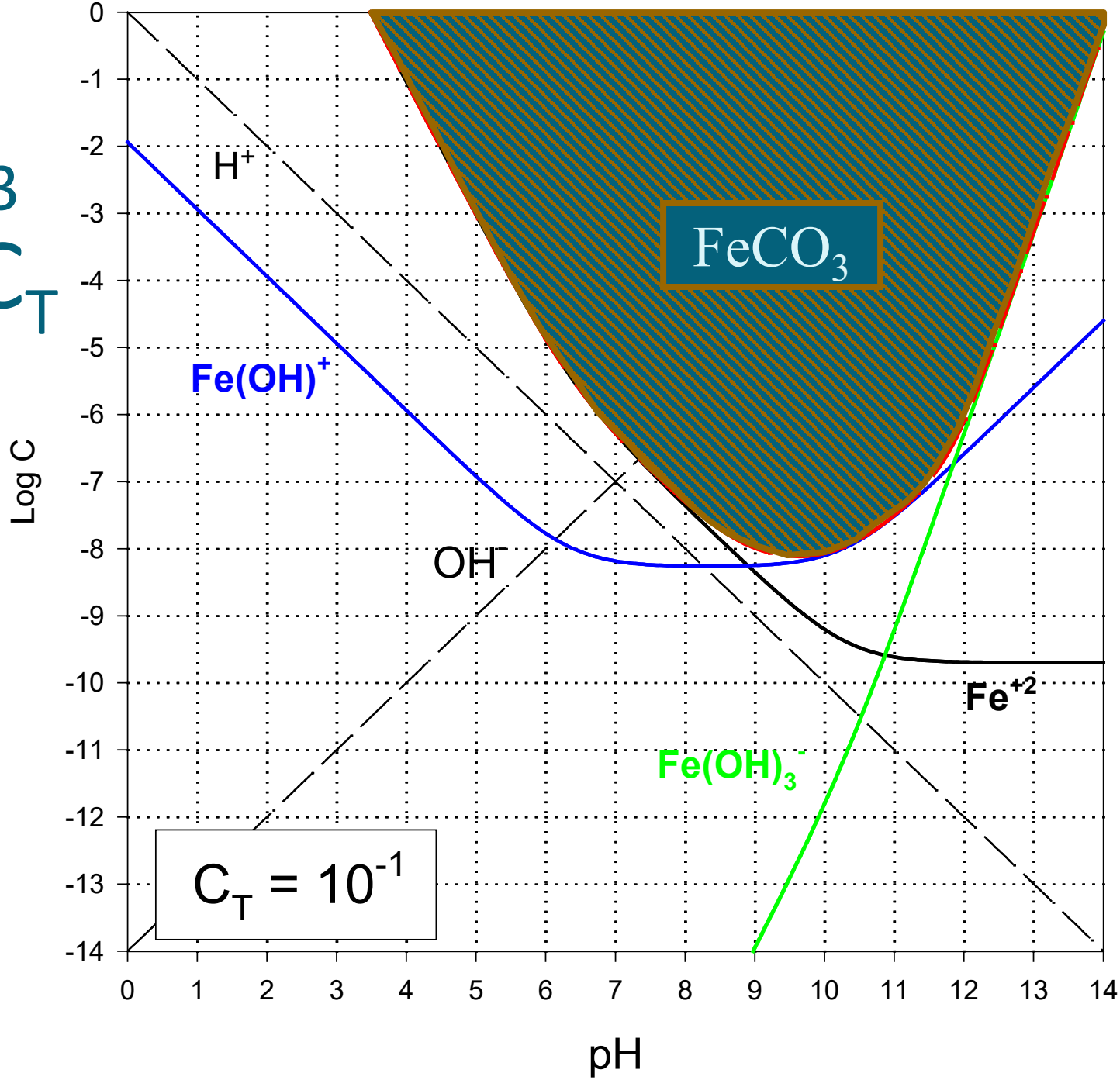
$FeCO_3$ mid C_T


FeCO3
H+
Fe(OH)+
Fe+2
OH-
Fe(OH)3-
CT = 10-3
Log C
pH
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14

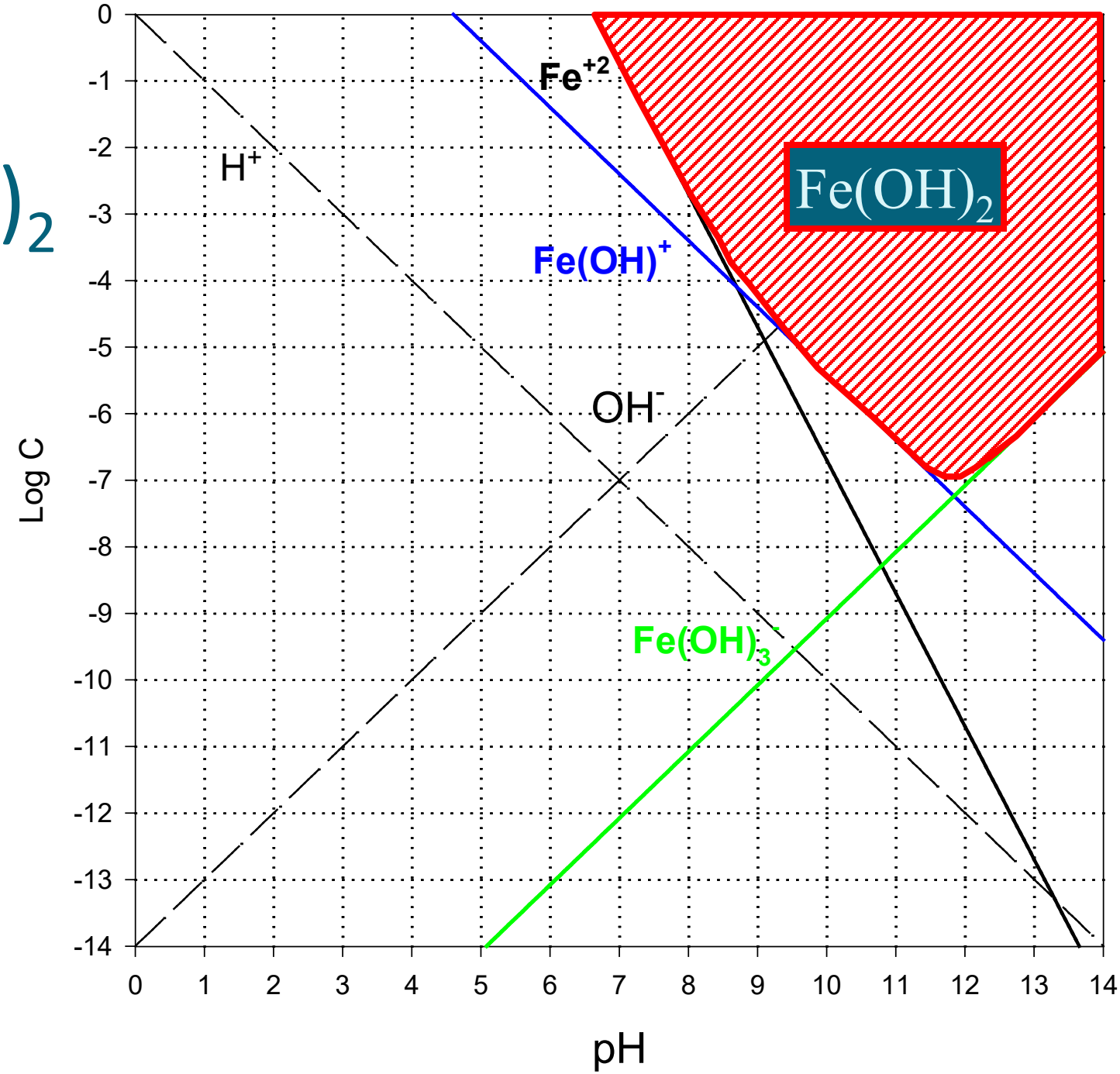
$FeCO_3$ low C_T


FeCO3
H+
Fe(OH)+
Fe+2
OH-
Fe(OH)3-
CT = 10-5
Log C
pH
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14

$FeCO_3$ high C_T



$Fe(OH)_2$



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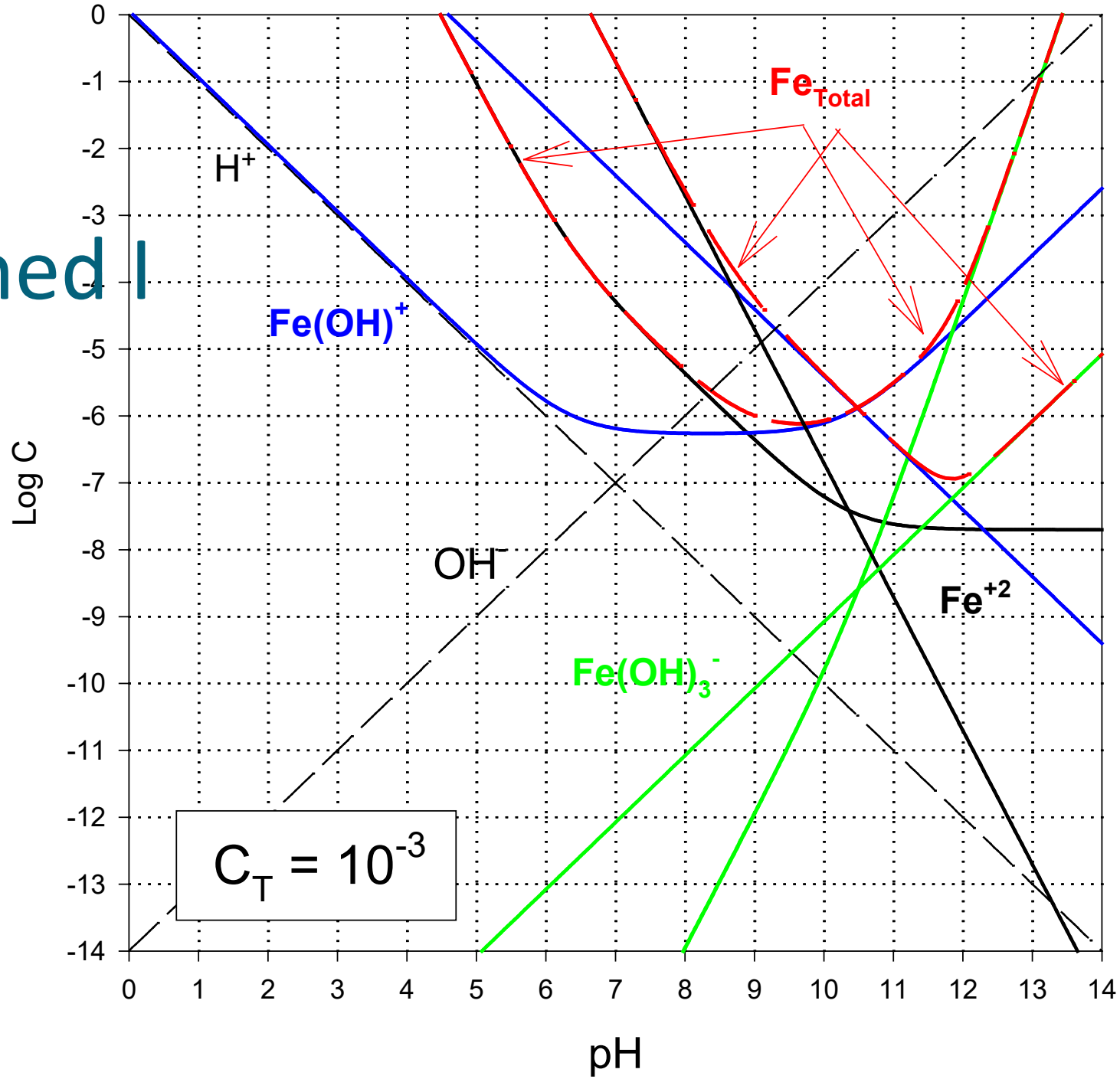
Mid C_T Combined I



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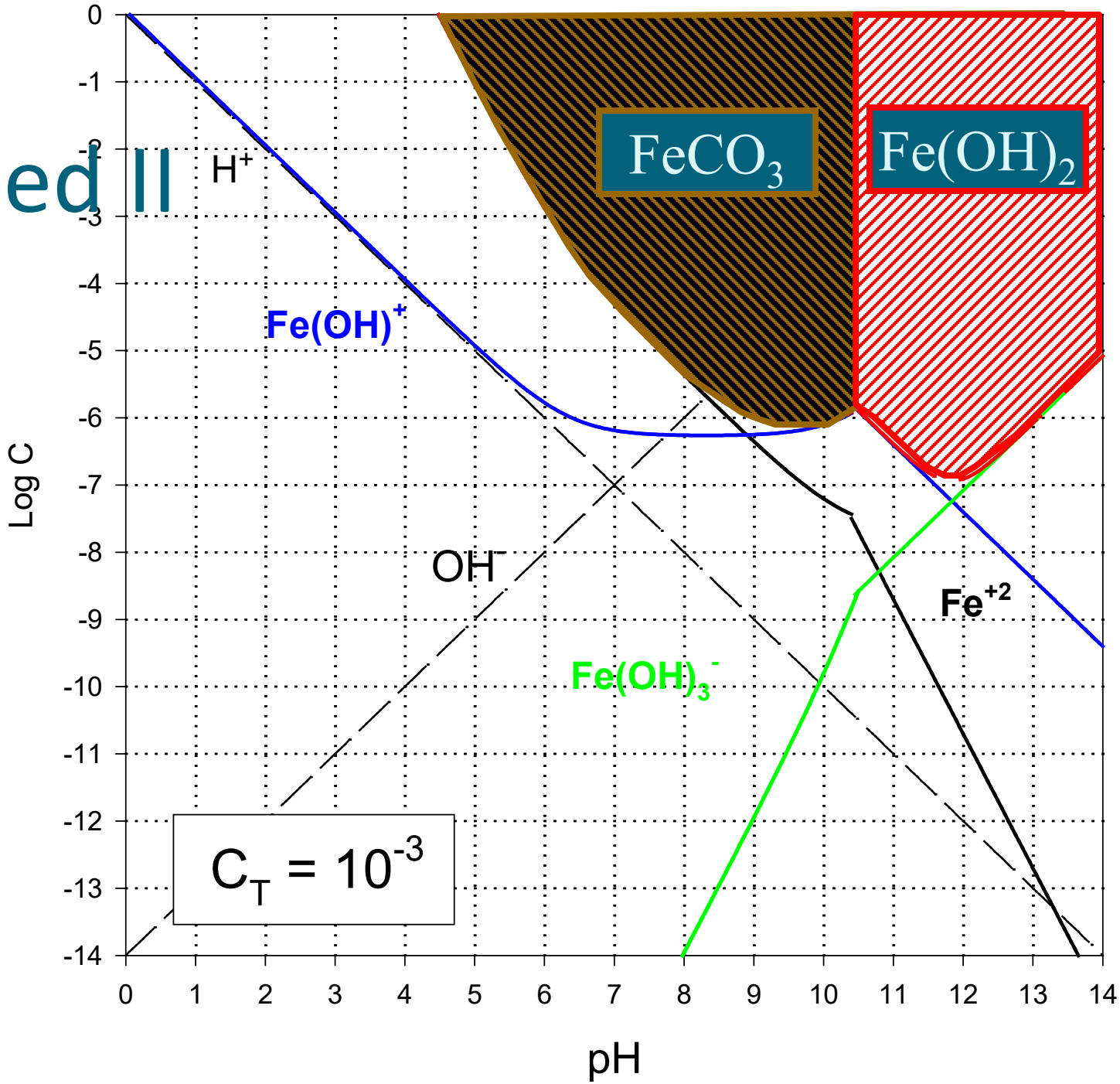
Combined II


FeCO3
Fe(OH)2
H+
Fe(OH)+
OH-
Fe+2
Fe(OH)3-
CT = 10-3
Log C
pH
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
0
1
2
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6
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9
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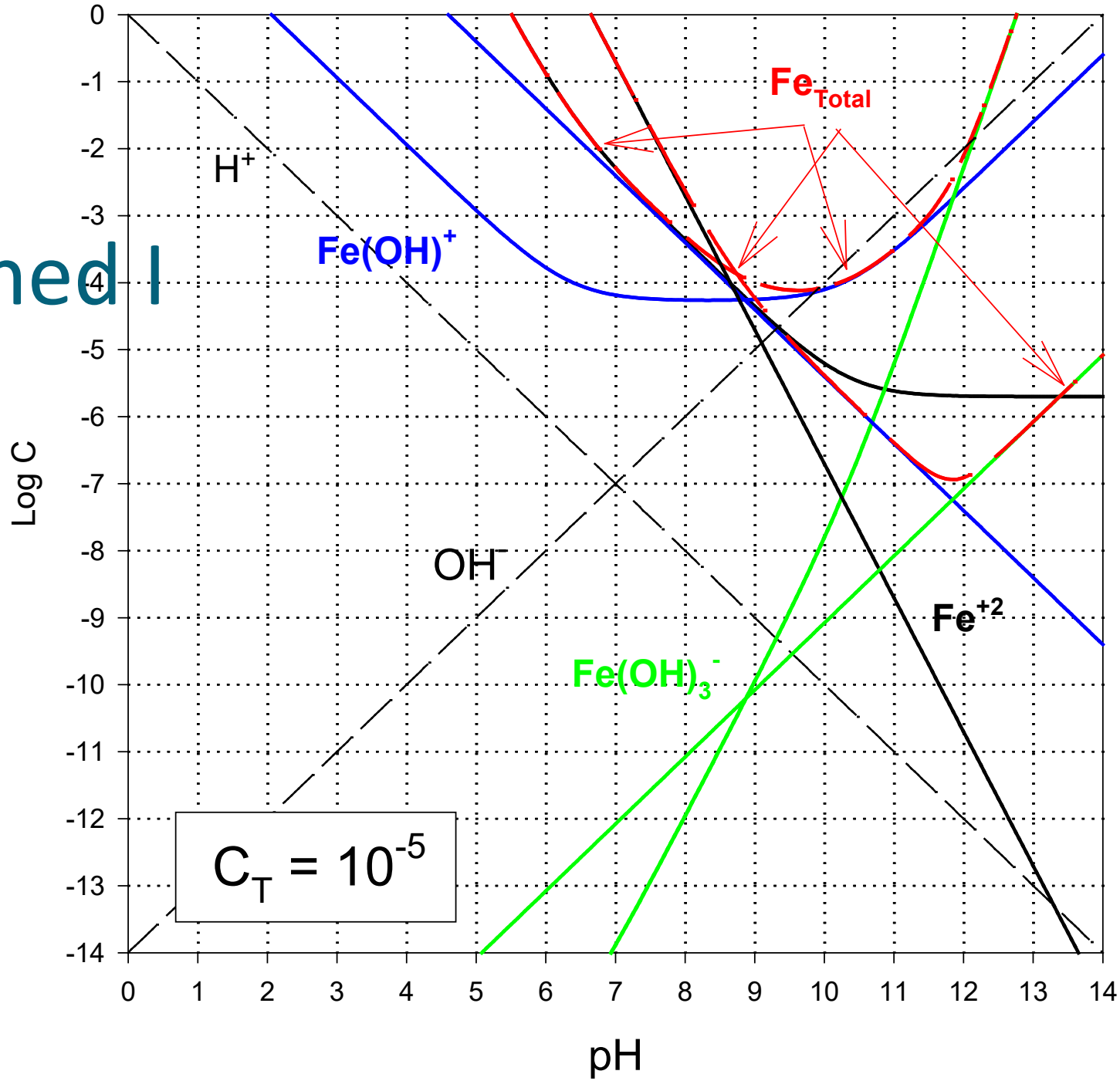
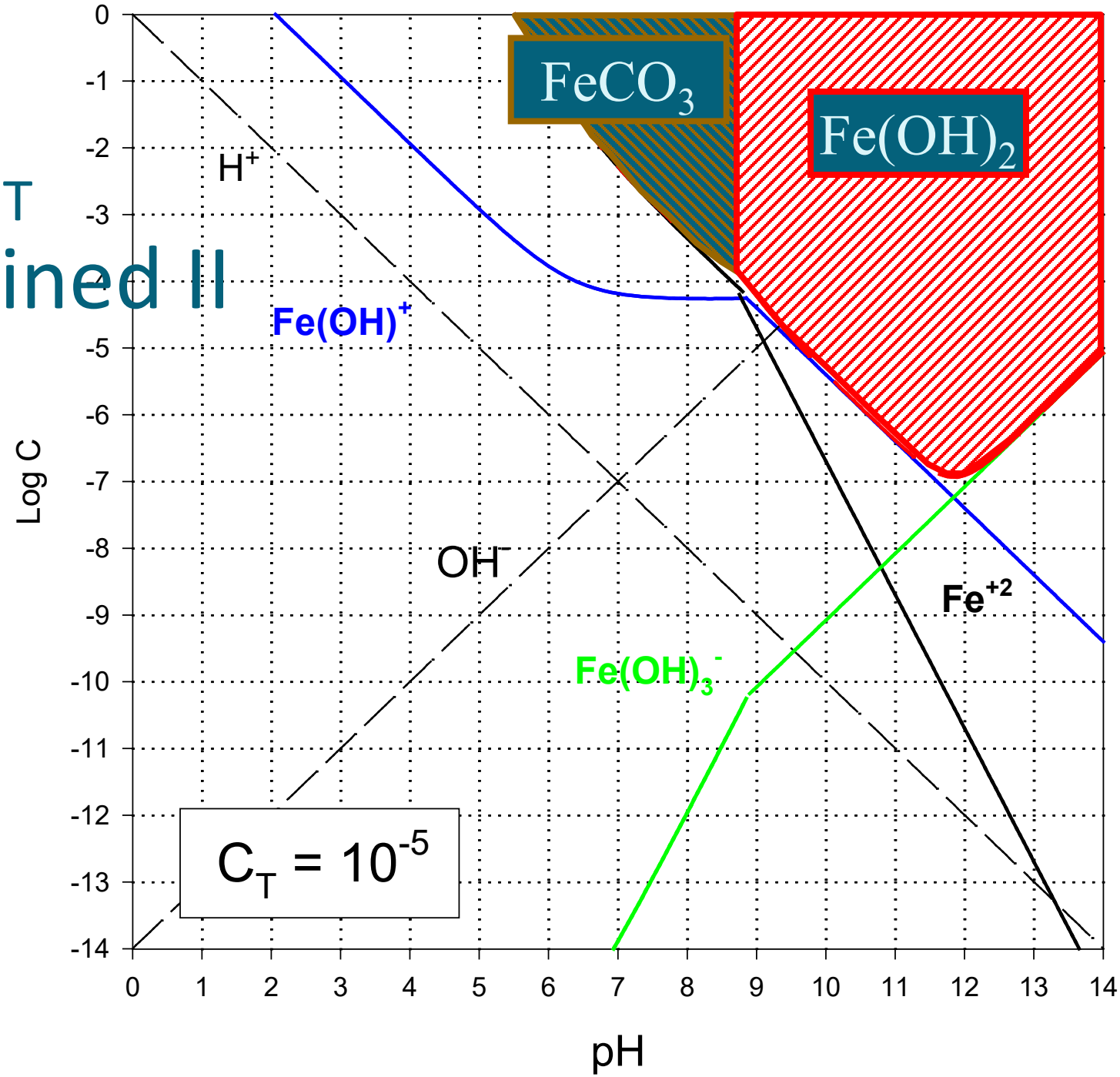
11
12
13
14

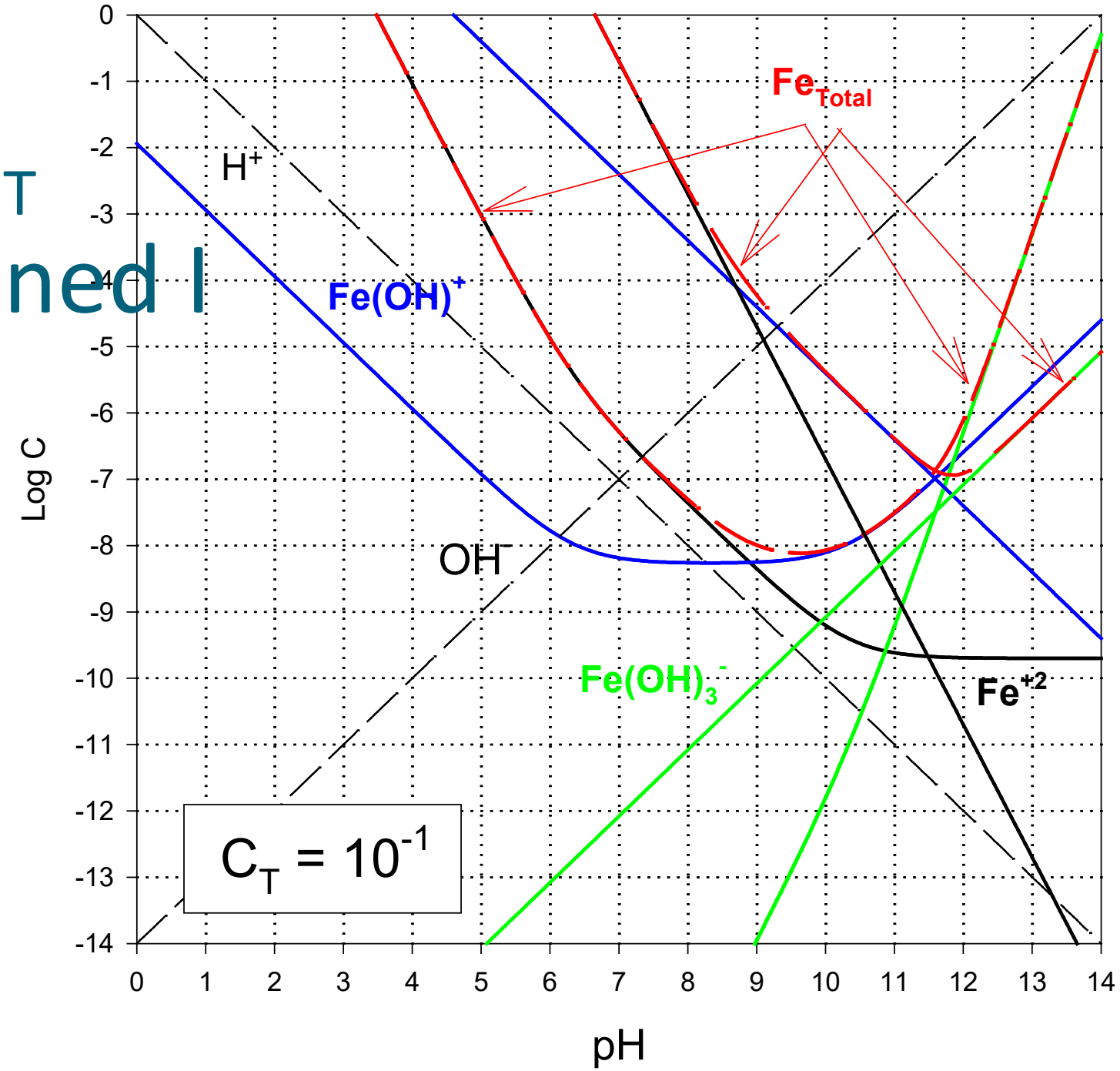
Low C_T Combined I



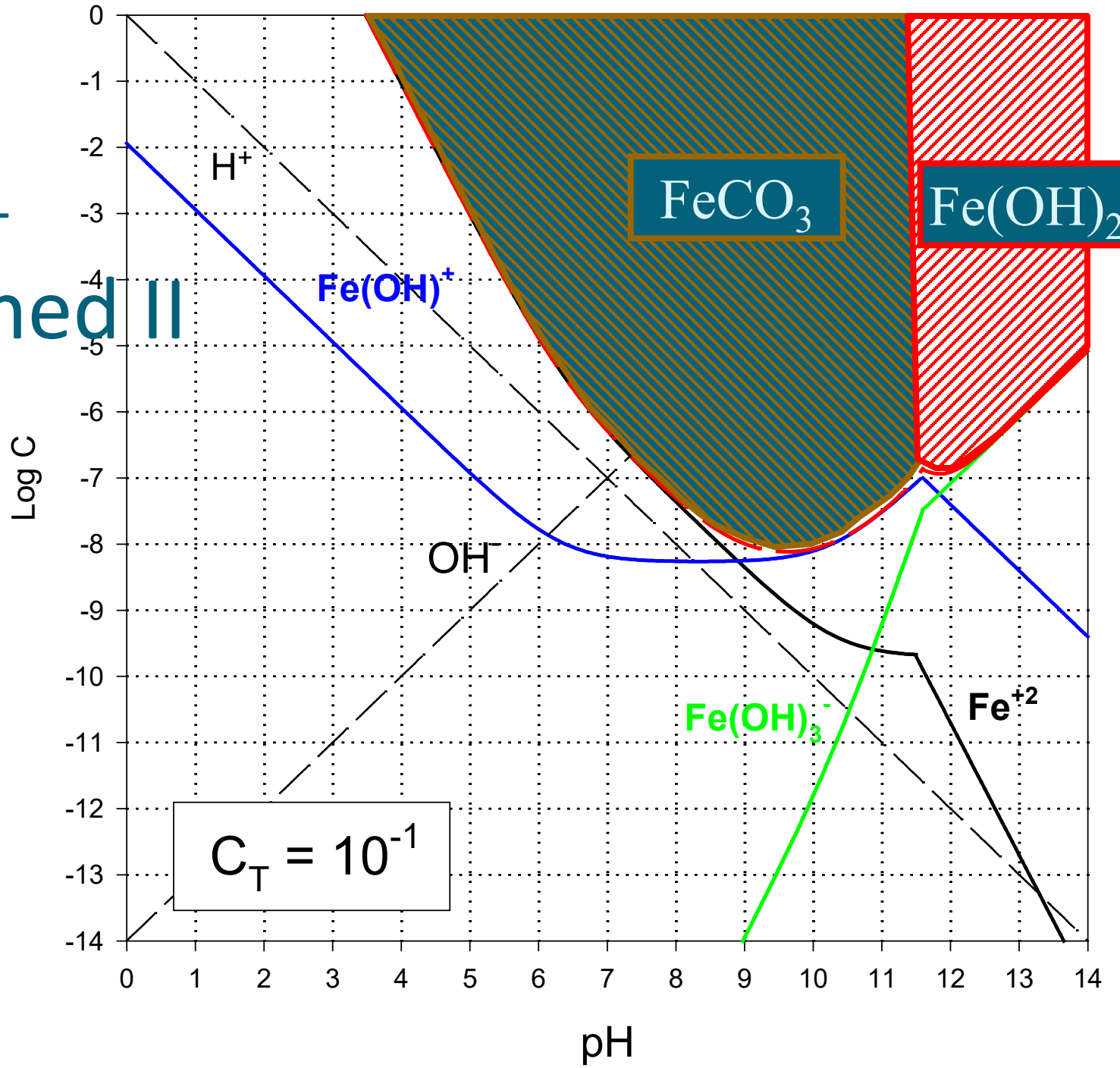
Low C_T Combined II



High C_T Combined I

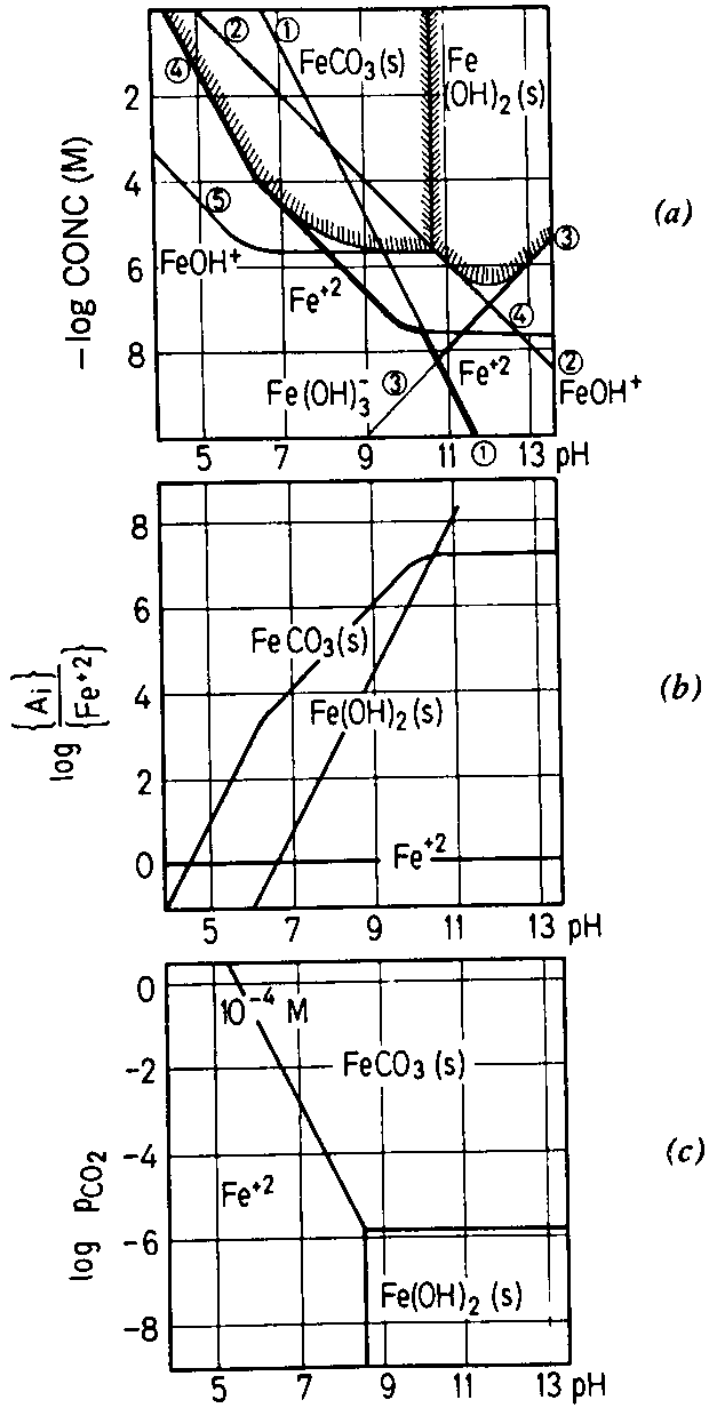


High C_T Combined II



Solubility & Domains

- A. solubility at $C_T=10^{-3}$ M
- B. activity ratio diagram at $C_T=10^{-3}$ M
- C. Predominance diagram for $Fe_T= 10^{-4}$ M



Stumm & Morgan, 1996, Figure 7.14, pg. 391

- To next lecture