

# CEE 680: Water Chemistry

Lecture #42

Precipitation and Dissolution: Iron &  
Predominance Diagrams

(Stumm & Morgan, Chapt.7)

**Benjamin; Chapter 8.7-8.15**

# Ferrous Hydroxide/Carbonate Equ.

- $\text{Fe(OH)}_2(\text{s}) = \text{Fe}^{+2} + 2\text{OH}^-$   $10^{-14.5}$
- $\text{Fe(OH)}_2(\text{s}) = \text{Fe(OH)}^+ + \text{OH}^-$   $10^{-9.4}$
- $\text{Fe(OH)}_2(\text{s}) + \text{OH}^- = \text{Fe(OH)}_3^-$   $10^{-5.1}$
  
- $\text{FeCO}_3(\text{s}) = \text{Fe}^{+2} + \text{CO}_3^-$   $10^{-10.7}$
- $\text{FeCO}_3(\text{s}) + \text{OH}^- = \text{Fe(OH)}^+ + \text{CO}_3^{-2}$   $10^{-5.6}$
- $\text{FeCO}_3(\text{s}) + 3\text{OH}^- = \text{Fe(OH)}_3^- + \text{CO}_3^{-2}$   $10^{-1.3}$

# Ferrous Hydroxide/Carbonate Equ.

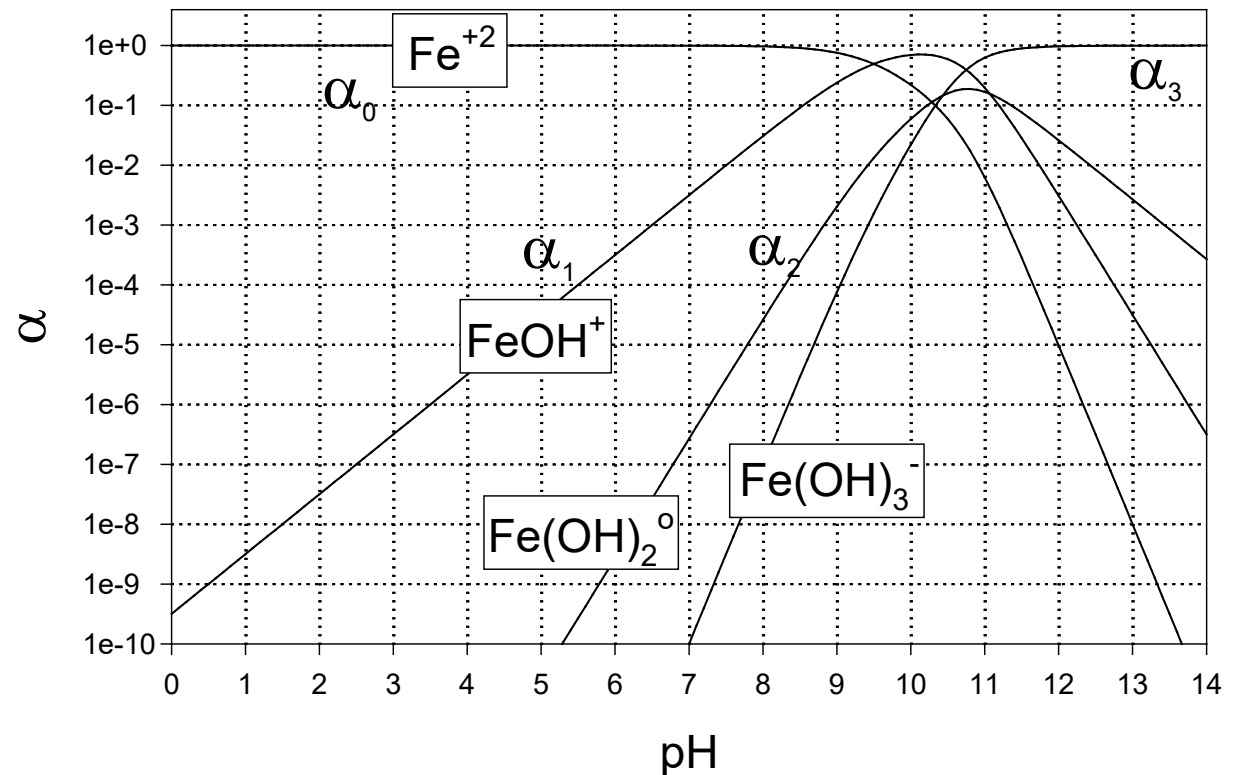
- $\text{Fe}(\text{OH})_2(\text{s}) = \text{Fe}^{+2} + 2\text{OH}^-$   $10^{-14.5}$
- $\text{Fe}(\text{OH})_2(\text{s}) = \text{Fe}(\text{OH})^+ + \text{OH}^-$   $10^{-9.4}$

$$\frac{\text{Fe}^{+2} + 2\text{OH}^-}{\text{Fe}(\text{OH})^+ + \text{OH}^-} = \frac{10^{-14.5}}{10^{-9.4}} = 10^{-5.1}$$

$$\frac{\text{Fe}^{+2}}{\text{Fe}(\text{OH})^+ + \text{H}^+} = 10^{+8.9}$$

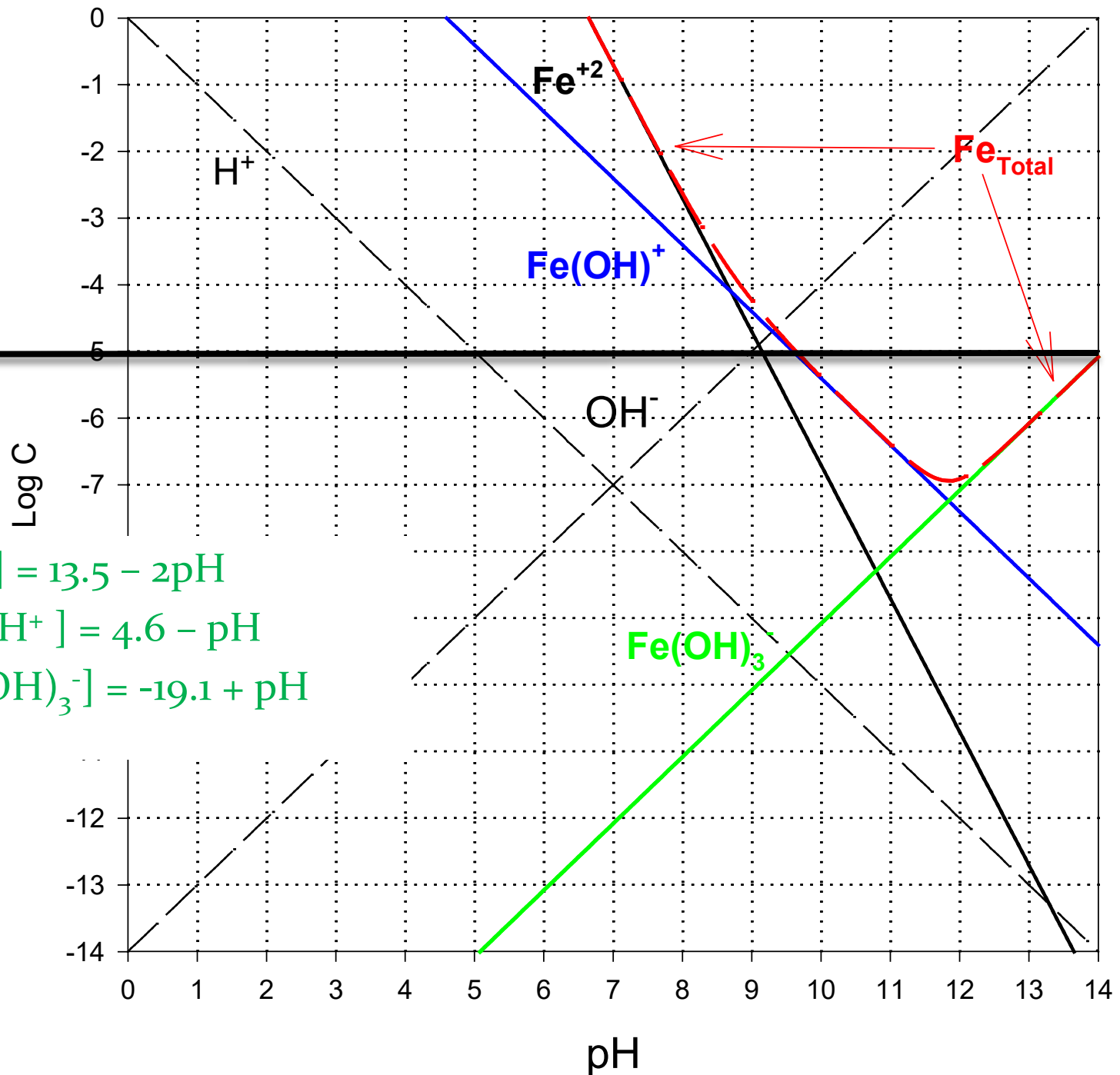
# Ferrous Hydroxides: $\alpha$ diagram

- Soluble predominance diagram



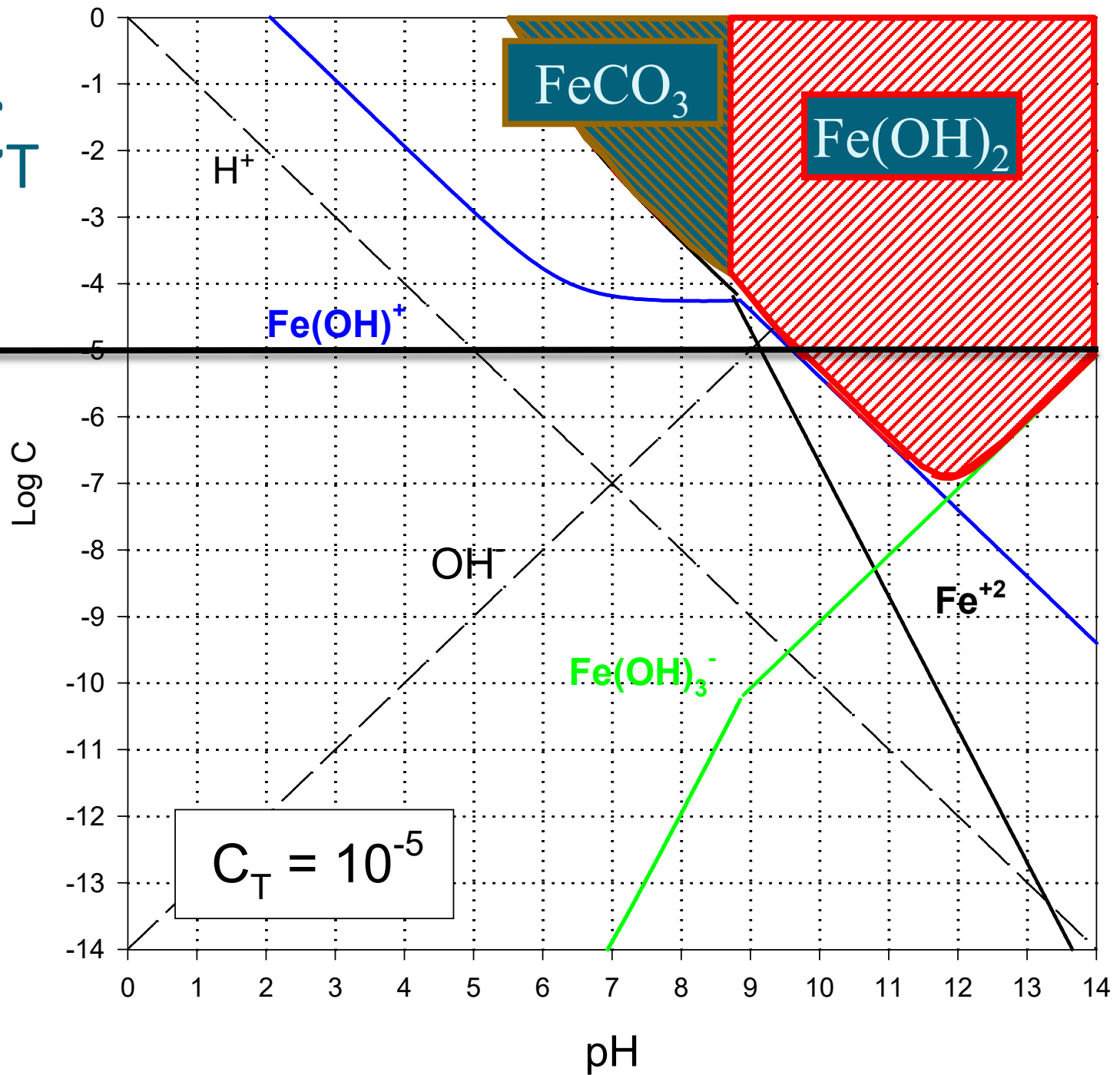
No  $C_T$

$10^{-5} Fe_T$  ←



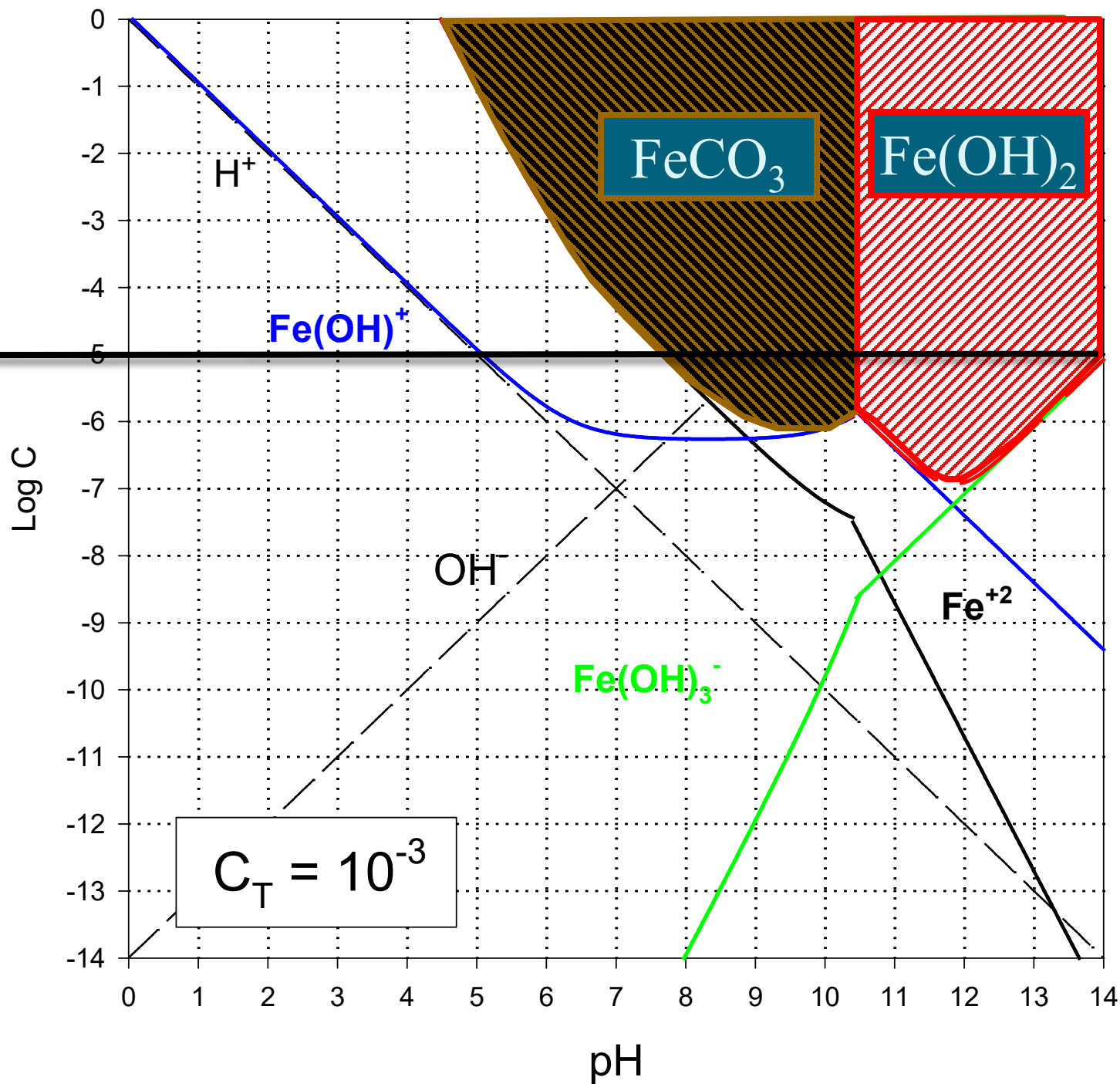
Low  $C_T$

$10^{-5} Fe_T$  ←



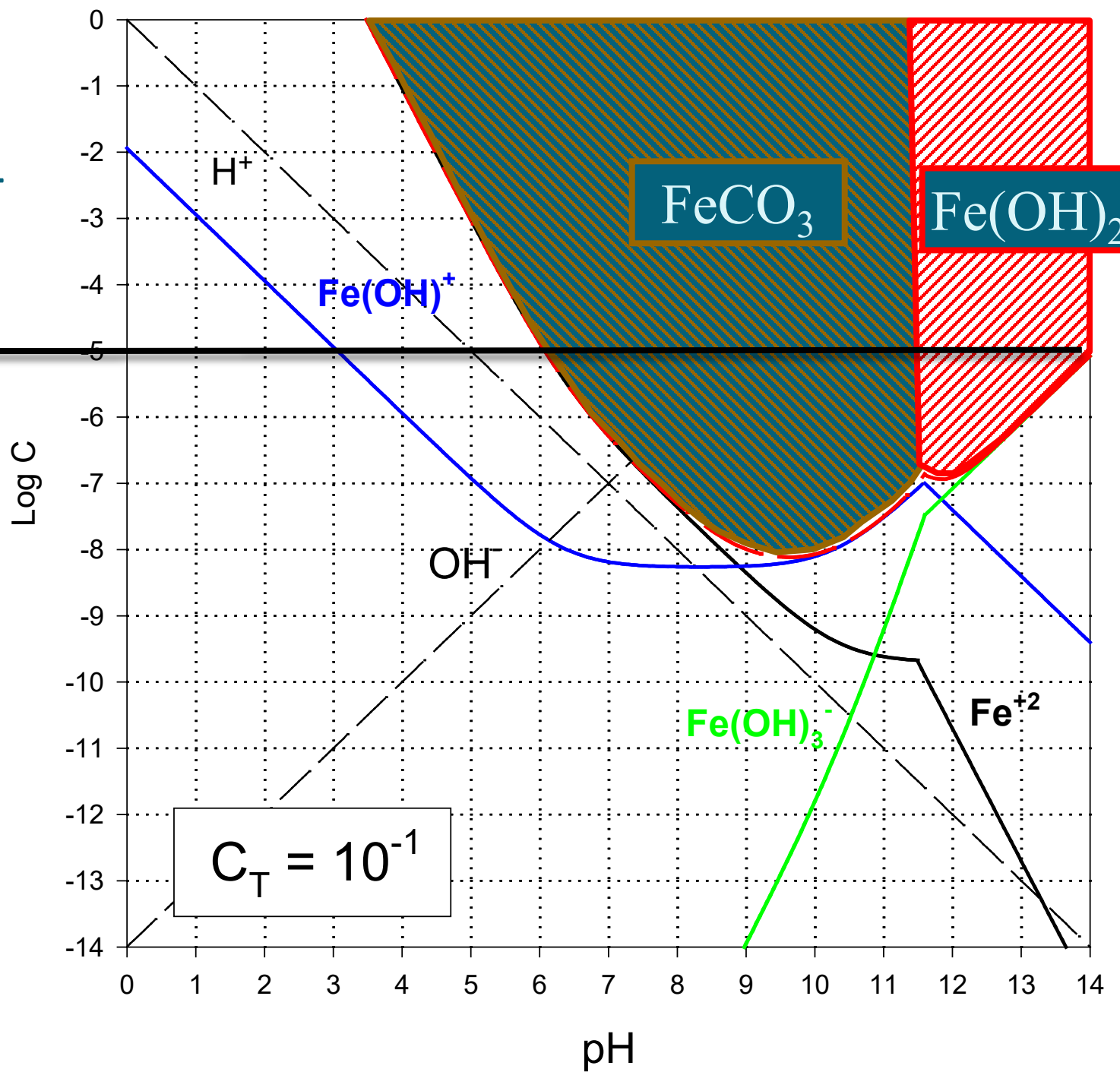
# Mid $C_T$

$10^{-5} Fe_T$  ←



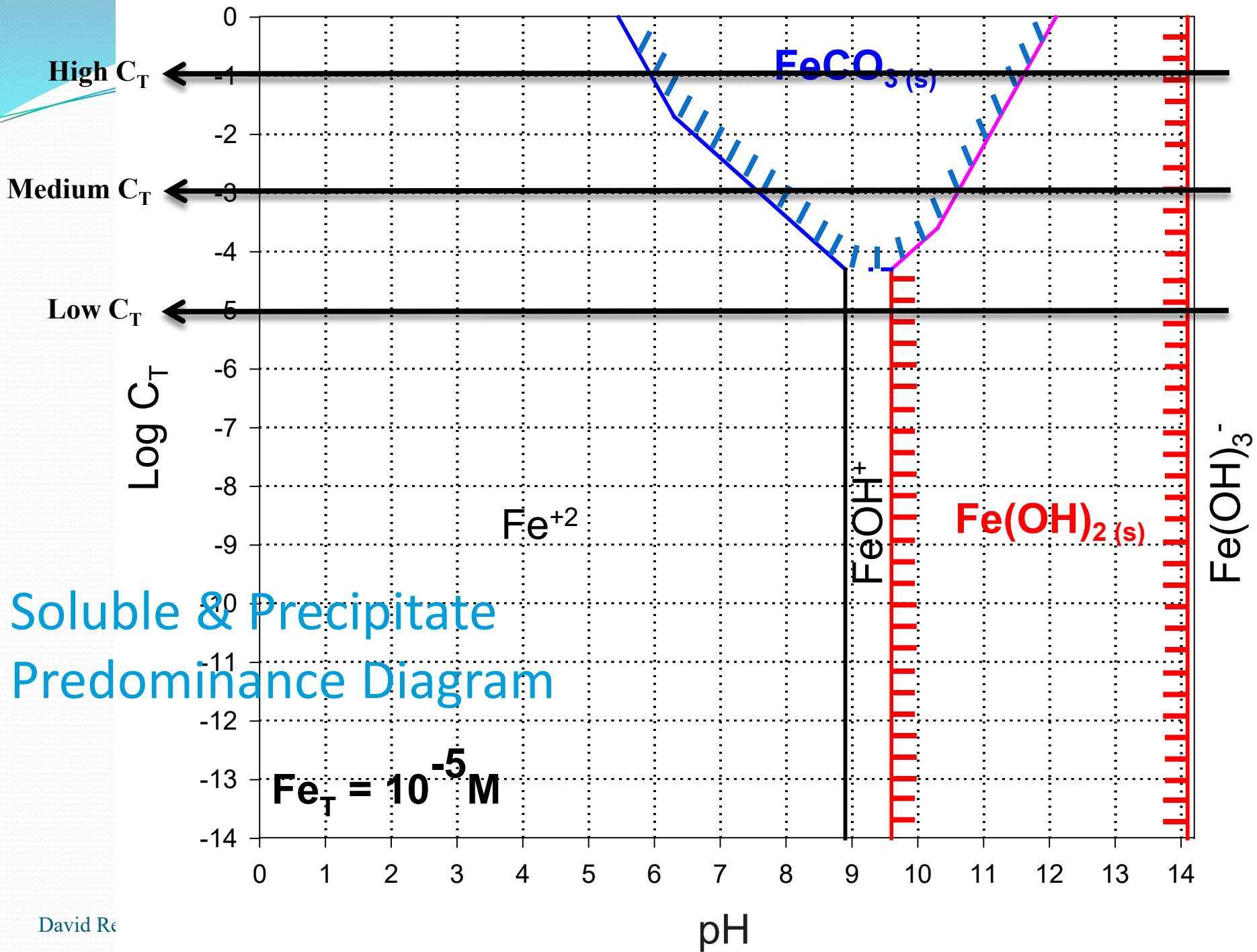
High  $C_T$

$10^{-5} Fe_T$  ←

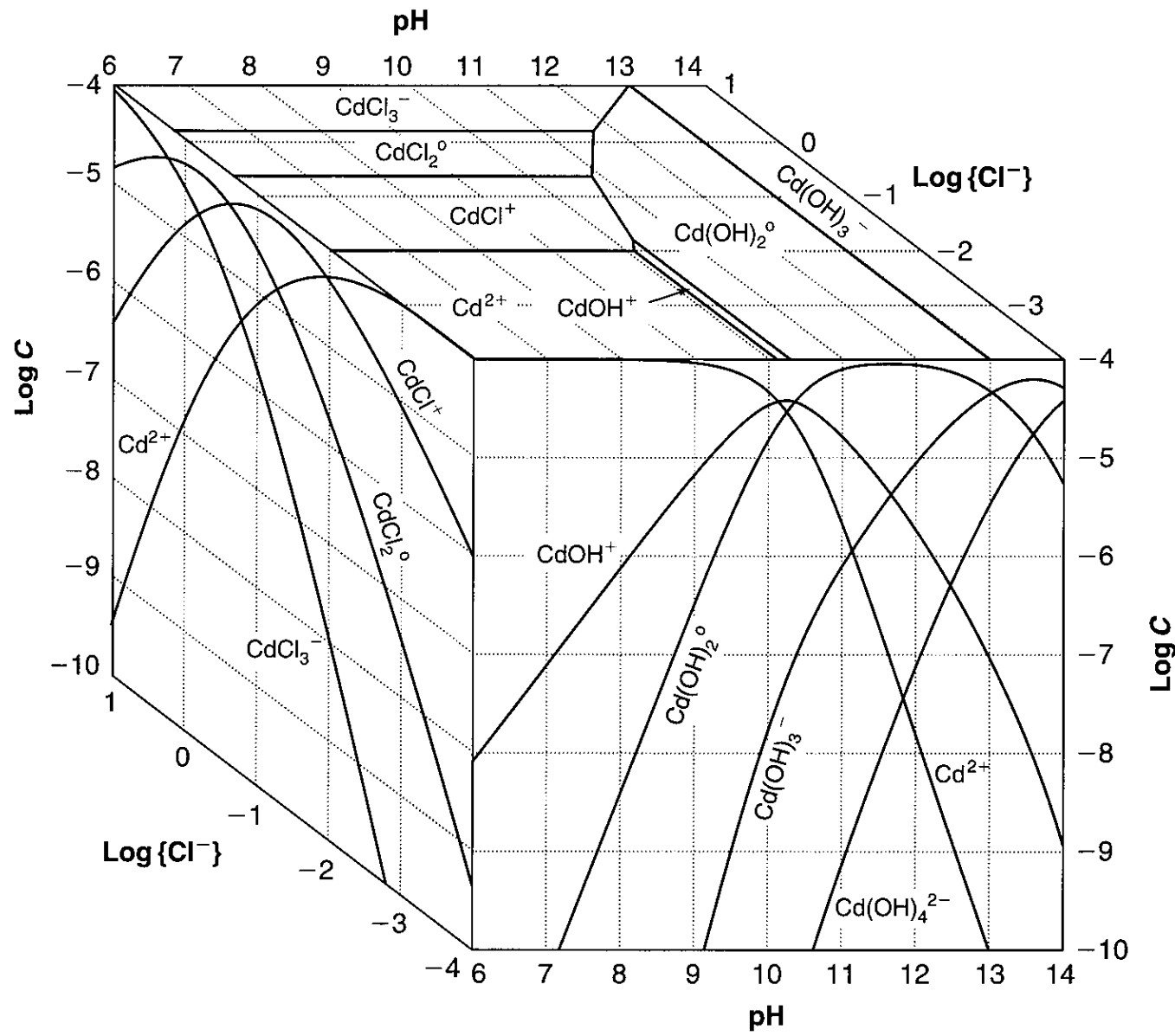




# Soluble & Precipitate Predominance Diagram



- Fig 8.7 in Benjamin

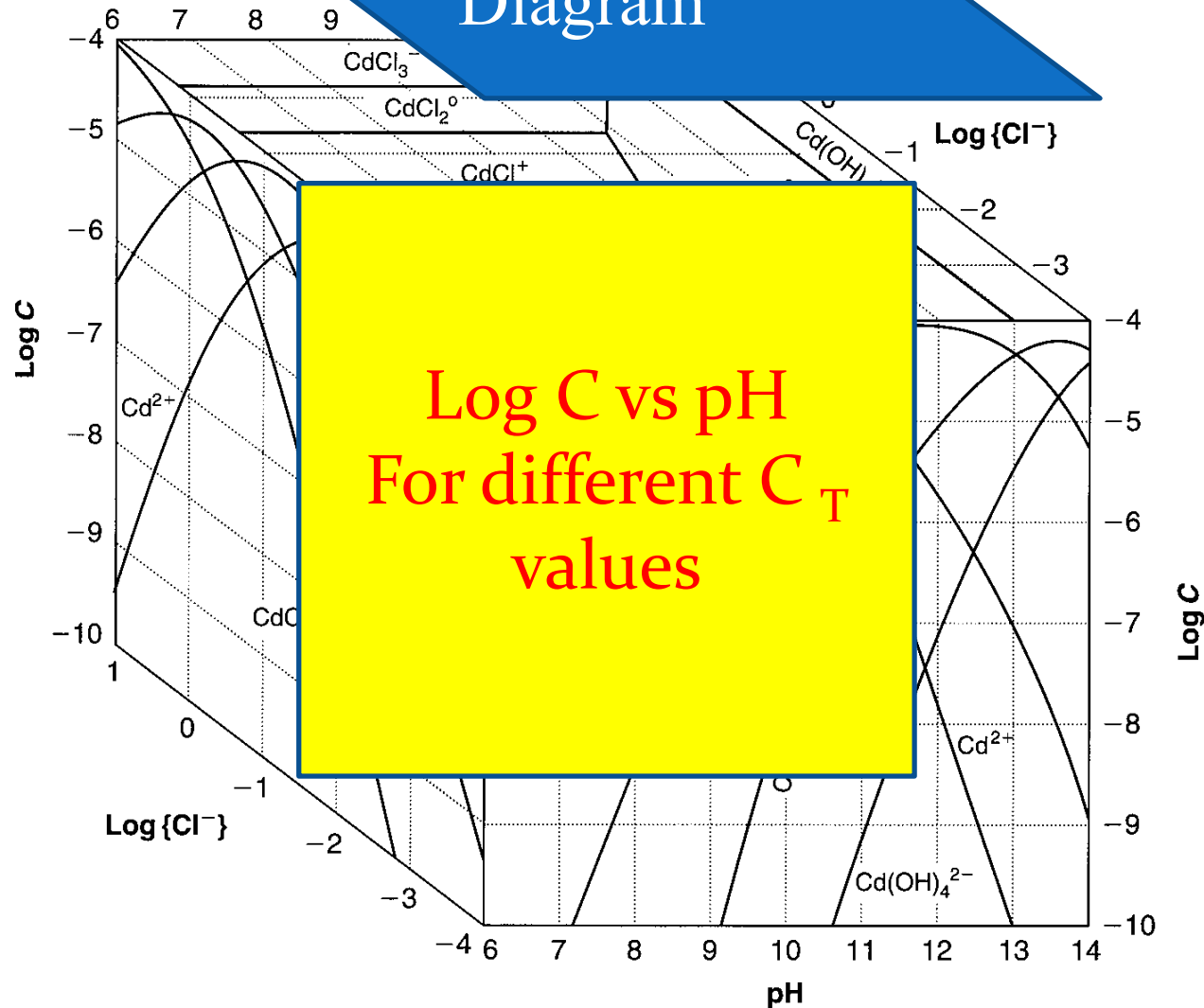


# 3-D form

## Predominance Diagram

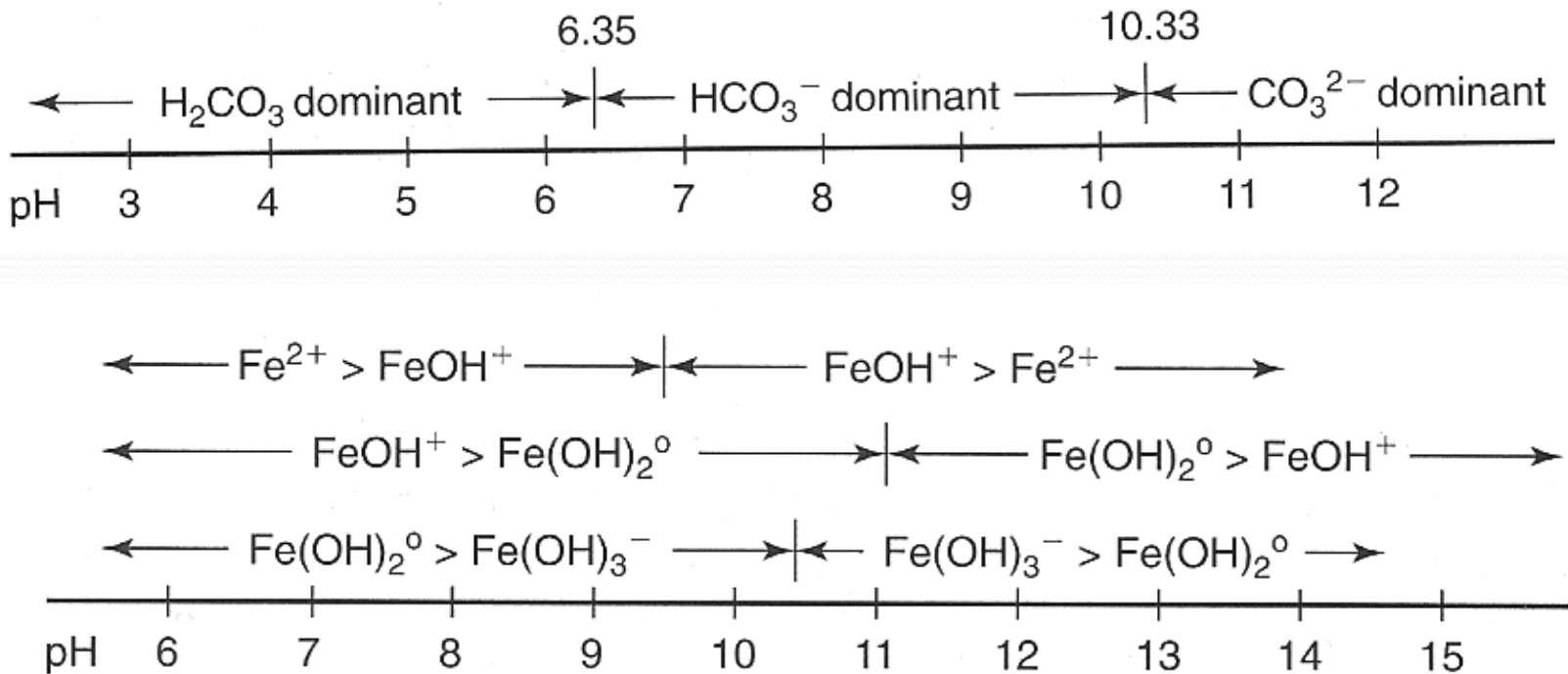
Fig. 2.7 in  
Benjamin

Log C  
vs  
Log C<sub>T</sub>



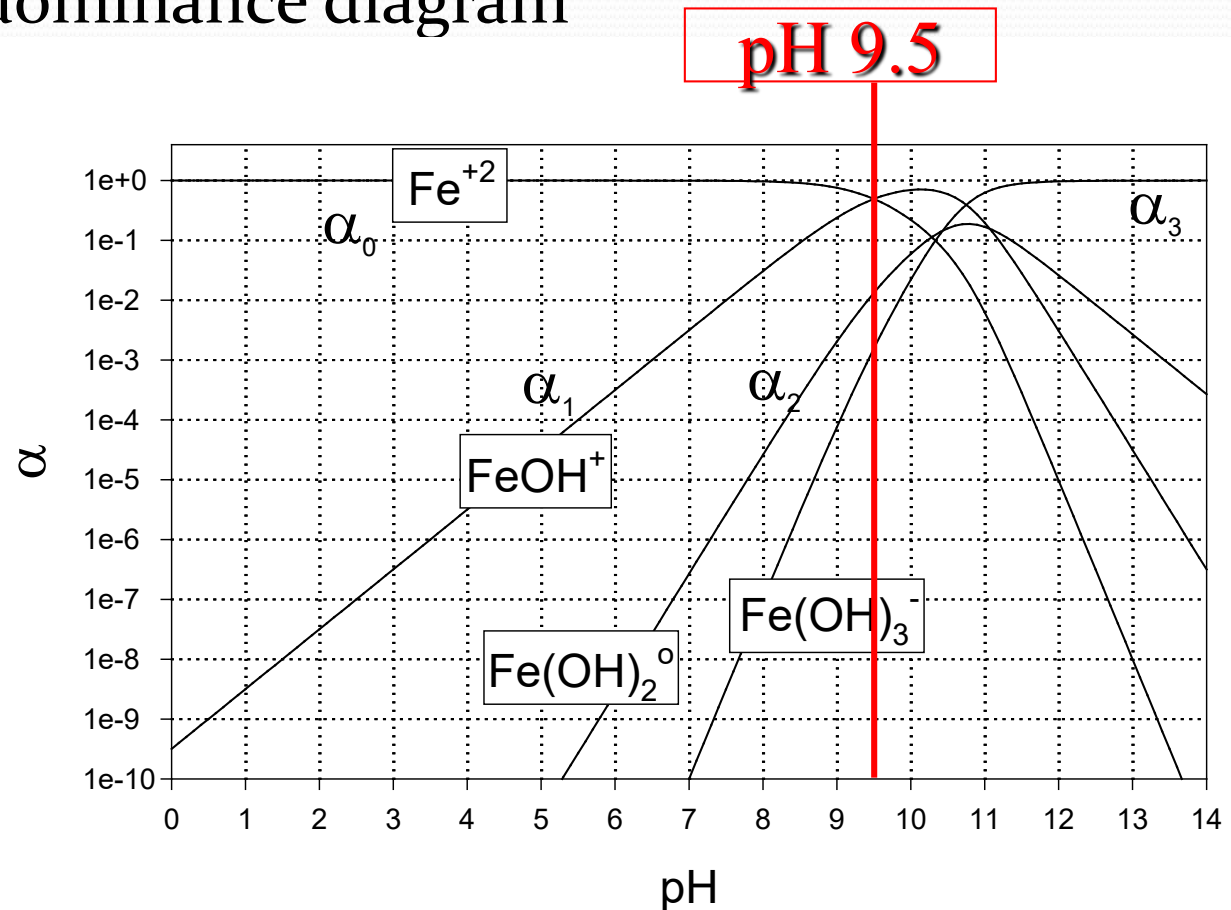
# Predominance Diagrams: Basics

- Soluble species

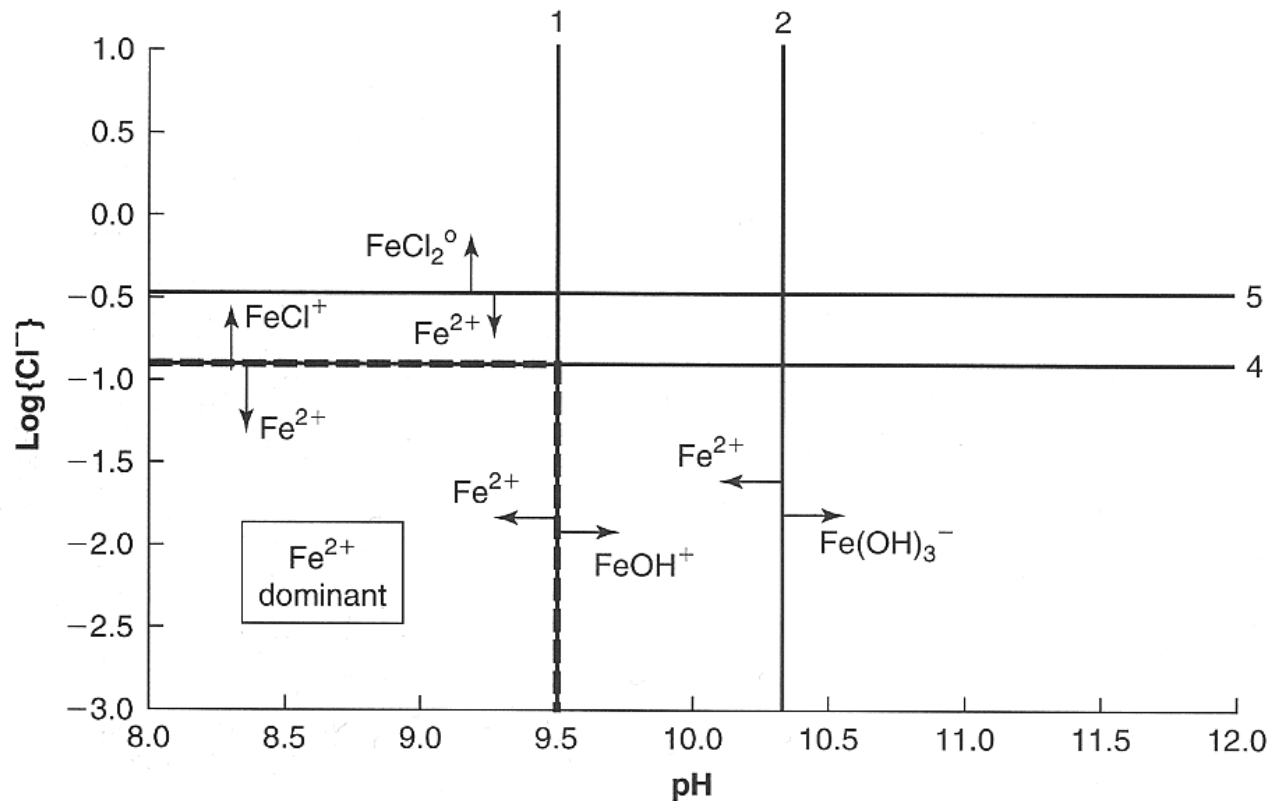


# Ferrous Hydroxides: $\alpha$ diagram

- Soluble predominance diagram

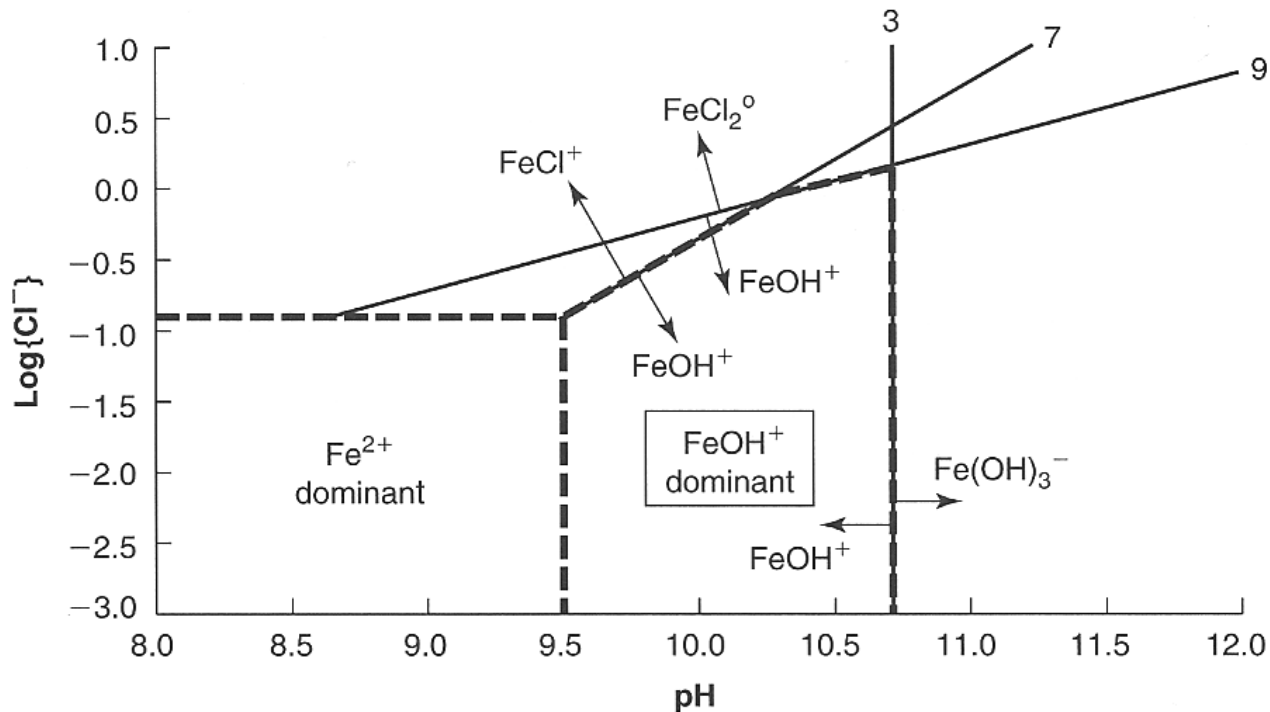


# Fe<sup>2+</sup>, Cl<sup>-</sup>, OH<sup>-</sup> system I



**Figure 8.8** Lines showing the four pairwise comparisons between Fe<sup>2+</sup> and other species in the example system. The arrows indicate the dominant species of the pair on each side of the line. The numbers correspond to the line number column in Table 8.6.

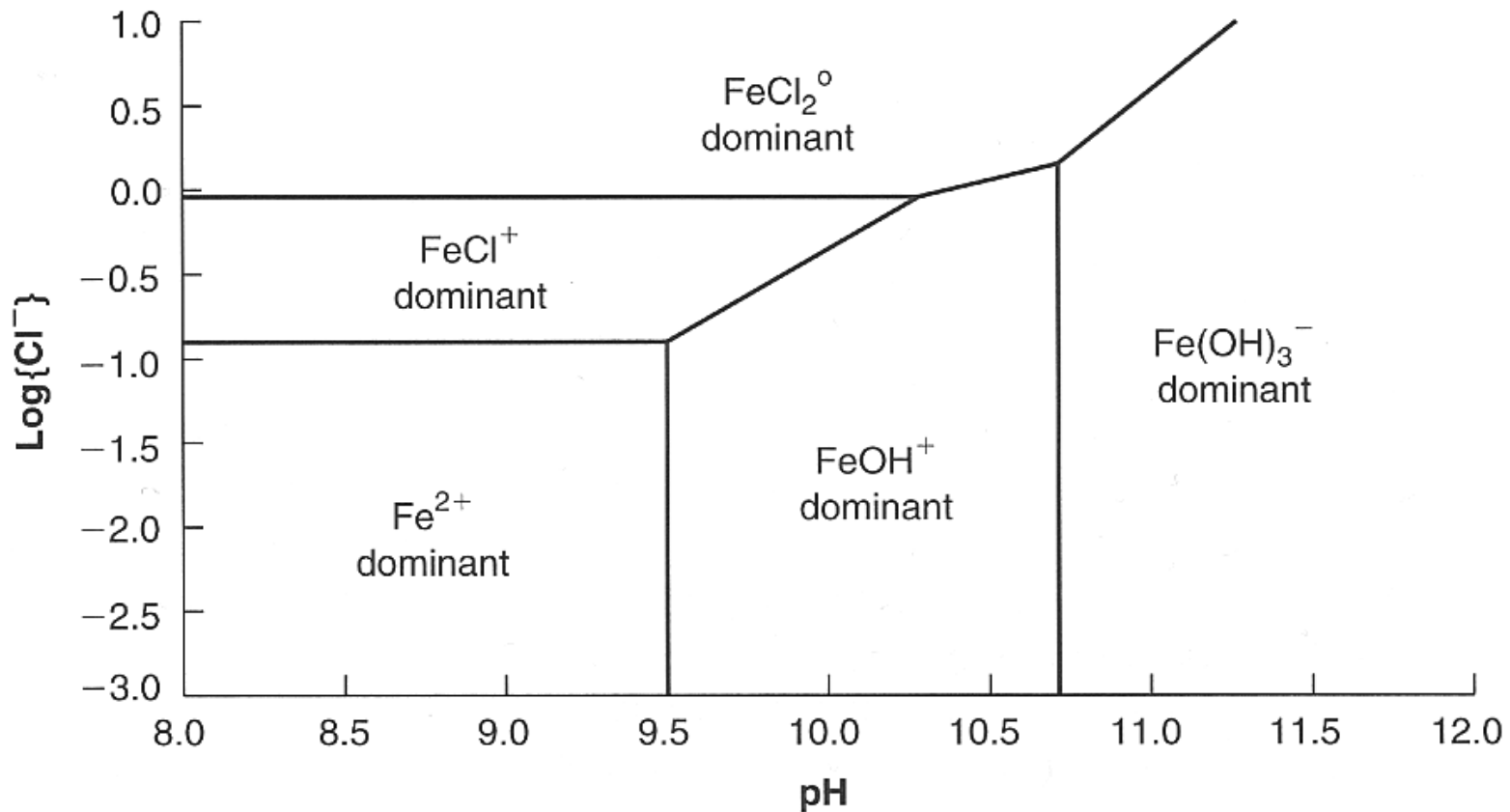
# Fe<sup>2+</sup>, Cl<sup>-</sup>, OH<sup>-</sup> system II



**Figure 8.9** Lines showing the pairwise comparisons between FeOH<sup>+</sup> and Fe(OH)<sub>2</sub><sup>0</sup>, FeCl<sup>+</sup>, or FeCl<sub>2</sub><sup>0</sup>, and the area of dominance of FeOH<sup>+</sup> inferred from those lines.

# Fe<sup>2+</sup>, Cl<sup>-</sup>, OH<sup>-</sup> system III

- Final predominance diagram
- Benjamin Figure 8.10, pg 391

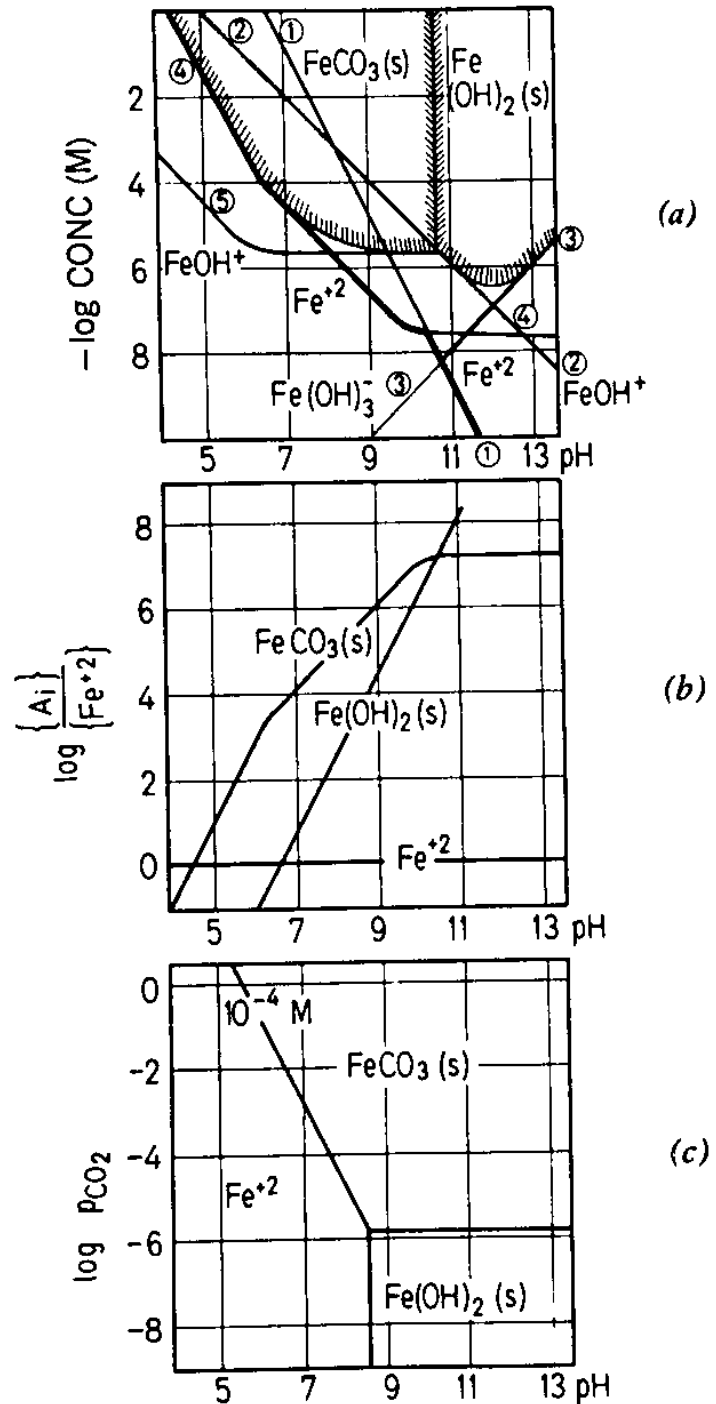




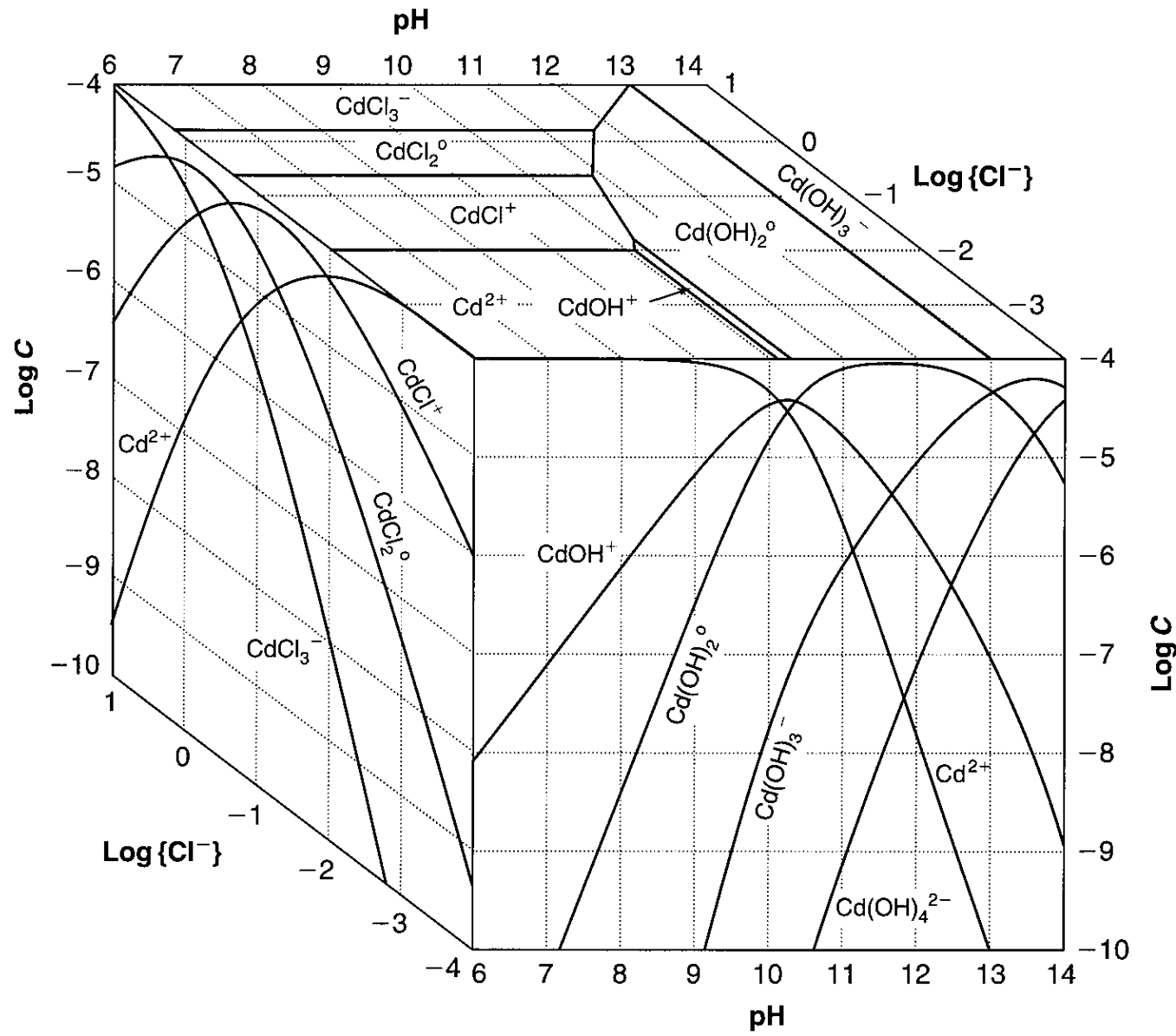
# Solubility & Domains

- **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



- Fig 8.7 in Benjamin



# Predominance Diagrams with Solid Phases

- Consider Ferrous Carbonate & Ferrous Hydroxide
  - $\text{Fe}_T = 10^{-5}$
- Closed System
  - On a  $\text{Log } C_T$  vs pH axis
- Open system
  - On a  $\text{Log } p_{\text{CO}_2}$  vs pH axis

# Predominance Diagrams: Guidance I

- Multiple levels



Benjamin, pg.391



CEE 680 web site

Increasing  
Complexity



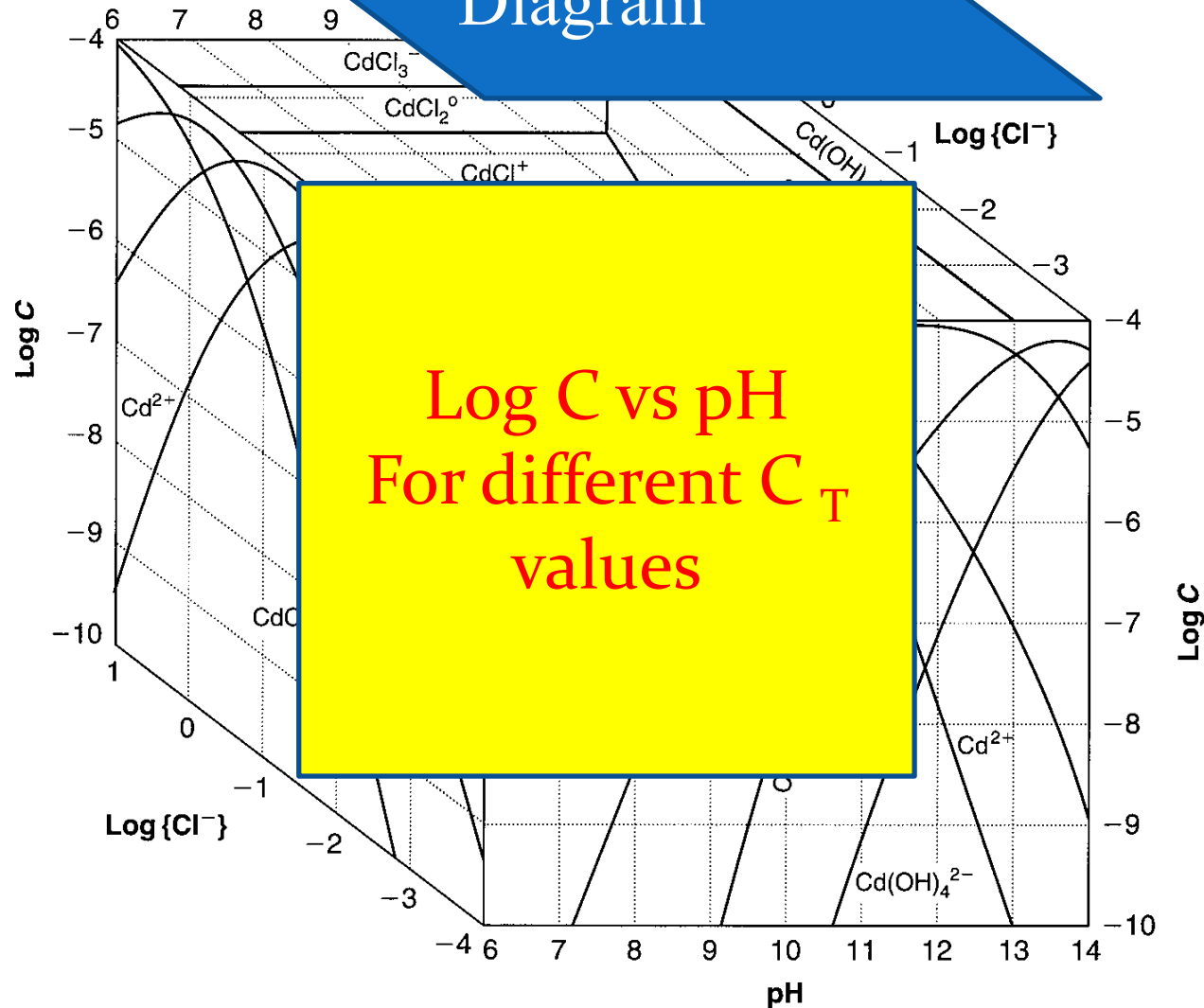
	No solids	1 solid	2 solids	>2 solids
Only OH complexes		Mg(OH) <sub>2</sub>		Alumino-silicates
Ligand complexes too	Fe <sup>+2</sup> /OH/ Cl <sup>-</sup>	Fe(OH) <sub>2</sub> , high Cl <sup>-</sup>		
pH-dependent ligand speciation			Fe(OH) <sub>2</sub> / FeCO <sub>3</sub>	
Complexing and pH-dependent ligand				

# 3-D form

## Predominance Diagram

Fig. 2.7 in  
Benjamin

Log C  
vs  
Log C<sub>T</sub>



# Predominance Diagrams: Guidance II

- Three types of lines
  - Type A: concerns soluble species only
    - defines where the two principal soluble species are at equal concentration in the no-precipitate zone
      - One predominates on the left side of the line, and the other on the right side
  - Type B: concerns one precipitate only
    - defines the “precipitate zone”, the boundary between precipitation and no precipitation
      - Where solubility criterion ( $Me_T$ ) can no longer be met
      - These depend on total soluble metal concentration
  - Type C: concerns two precipitates
    - defines boundary between two different solid phases (precipitates)

# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example I

- Type A lines: concern soluble species
  - Fe<sup>+2</sup> to Fe(OH)<sup>+</sup>
    - use first 2 equilibria
    - set species equal to each other

$$10^{-14.5} = [Fe^{+2}][OH^{-}]^2$$

$$[Fe^{+2}] = \frac{10^{-14.5}}{[OH^{-}]^2}$$

$$10^{-9.4} = [FeOH^{+}][OH^{-}]$$

$$[FeOH^{+}] = \frac{10^{-9.4}}{[OH^{-}]}$$

$$\frac{10^{-14.5}}{[OH^{-}]^2} = \frac{10^{-9.4}}{[OH^{-}]}$$

$$10^{-14.5} = 10^{-9.4}[OH^{-}] = 10^{-9.4}K_w/[H^{+}]$$

$$[H^{+}] = 10^{+14.5}10^{-9.4}10^{-14} = 10^{-8.9}$$

$$pH = 8.9$$

**Equation #A1**

# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example II

- Type A lines: concern soluble species
  - Fe(OH)<sup>+</sup> to Fe(OH)<sub>3</sub><sup>-</sup>
    - use 2<sup>nd</sup> & 3<sup>rd</sup> equilibria
    - set species equal to each other

$$10^{-9.4} = [FeOH^+][OH^-]$$

$$[FeOH^+] = \frac{10^{-9.4}}{[OH^-]}$$

$$10^{-5.1} = \frac{[Fe(OH)_3^-]}{[OH^-]}$$

$$[Fe(OH)_3^-] = 10^{-5.1}[OH^-]$$

$$\frac{10^{-9.4}}{[OH^-]} = 10^{-5.1}[OH^-]$$

$$10^{-9.4} = 10^{-5.1}[OH^-]^2 = 10^{-5.1} K_w^2 / [H^+]^2$$

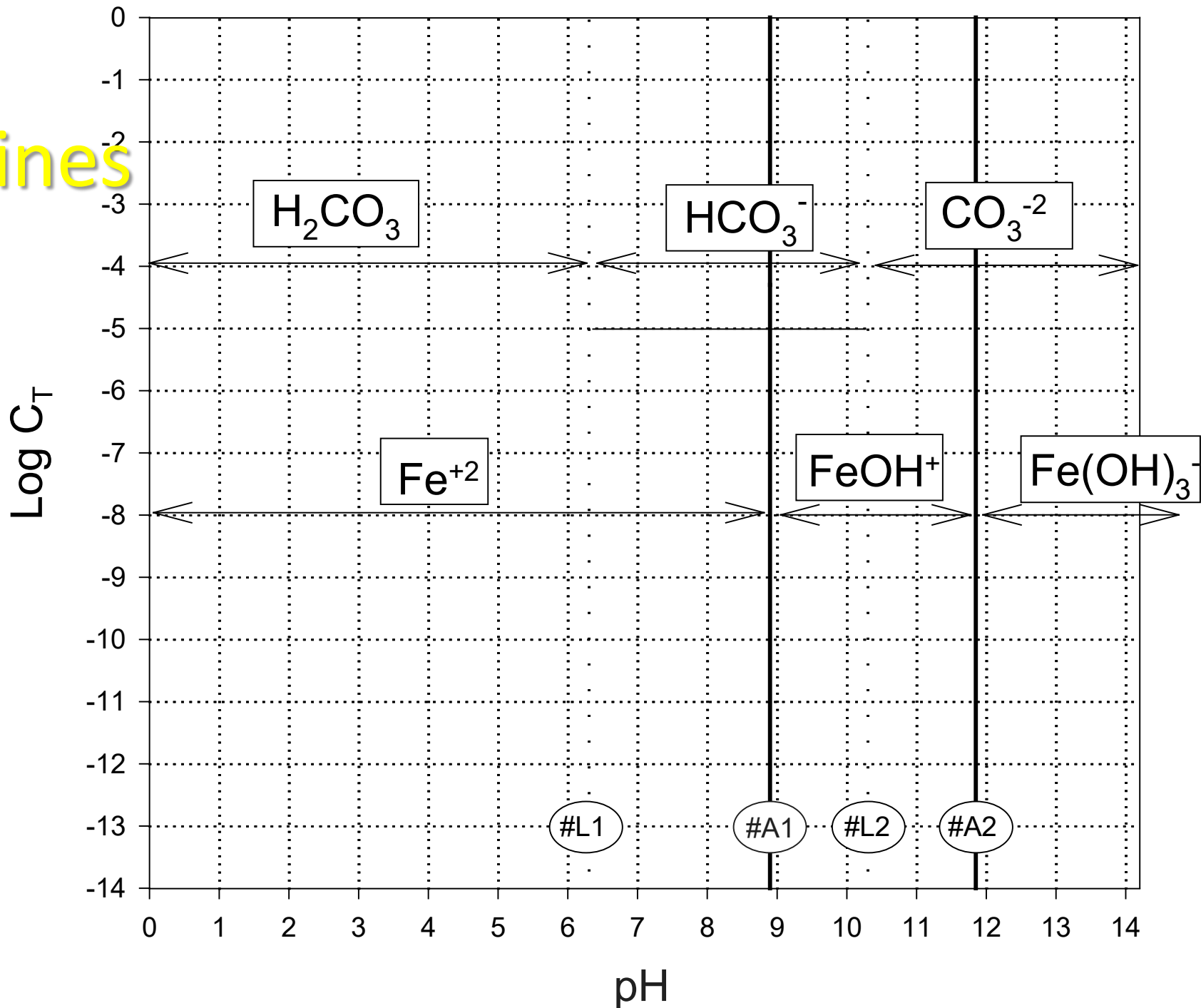
$$[H^+]^2 = 10^{-5.1} 10^{-28} 10^{+9.4} = 10^{-23.7}$$

$$pH = 11.85$$

→ **Equation #A2**



# A lines



# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example III

- Type B lines: concern one precipitate
  - Fe(OH)<sub>2(s)</sub>
    - First look at Fe<sup>+2</sup> and the precipitate

$$10^{-14.5} = [Fe^{+2}][OH^{-}]^2 = [Fe^{+2}] \left( \frac{K_w^2}{[H^+]^2} \right)$$
$$[H^+]^2 = 10^{+14.5} K_w^2 [Fe^{+2}] = 10^{-13.5} [Fe^{+2}]$$
$$pH = 6.75 - \frac{1}{2} \log [Fe^{+2}]$$

And assuming,

$$[Fe^{+2}] \approx Fe_T = 10^{-5},$$

Then:

$$pH = 6.75 + 2.5$$
$$= 9.25$$

But Fe(OH)<sup>+</sup> predominates @ pH=8.9-11.85, so this assumption is **invalid!**

# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example IV

- Type B lines: concern one precipitate

- Fe(OH)<sub>2(s)</sub>
  - Next look at FeOH<sup>+</sup> and the precipitate

$$10^{-9.4} = [FeOH^+][OH^-] = [FeOH^+] \left( \frac{K_w}{[H^+]} \right)$$
$$[H^+] = 10^{+9.4} K_w [FeOH^+] = 10^{-4.6} [FeOH^+]$$
$$pH = 4.6 - \log[FeOH^+]$$

Again Fe(OH)<sup>+</sup> predominates @ pH=8.9-11.85, so now this assumption is valid.

And assuming,  
[FeOH<sup>+</sup>] ≈ Fe<sub>T</sub> = 10<sup>-5</sup>,  
Then:

$$pH = 4.6 + 5.0$$

$$pH = 9.6$$

**Equation #B1**

# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example V

- Type B lines: concern one precipitate

- Fe(OH)<sub>2(s)</sub>
  - Next look at Fe(OH)<sub>3</sub><sup>-</sup> and the precipitate

$$10^{-5.1} = \frac{[Fe(OH)_3^-]}{[OH^-]} = [Fe(OH)_3^-] \left( \frac{[H^+]}{K_w} \right)$$

$$[H^+] = 10^{-5.1} K_w [Fe(OH)_3^-]^{-1} = 10^{-19.1} [Fe(OH)_3^-]$$

$$pH = 19.1 + \log[Fe(OH)_3^-]$$

And assuming,

$$[Fe(OH)_3^-] \approx Fe_T = 10^{-5},$$

Then:

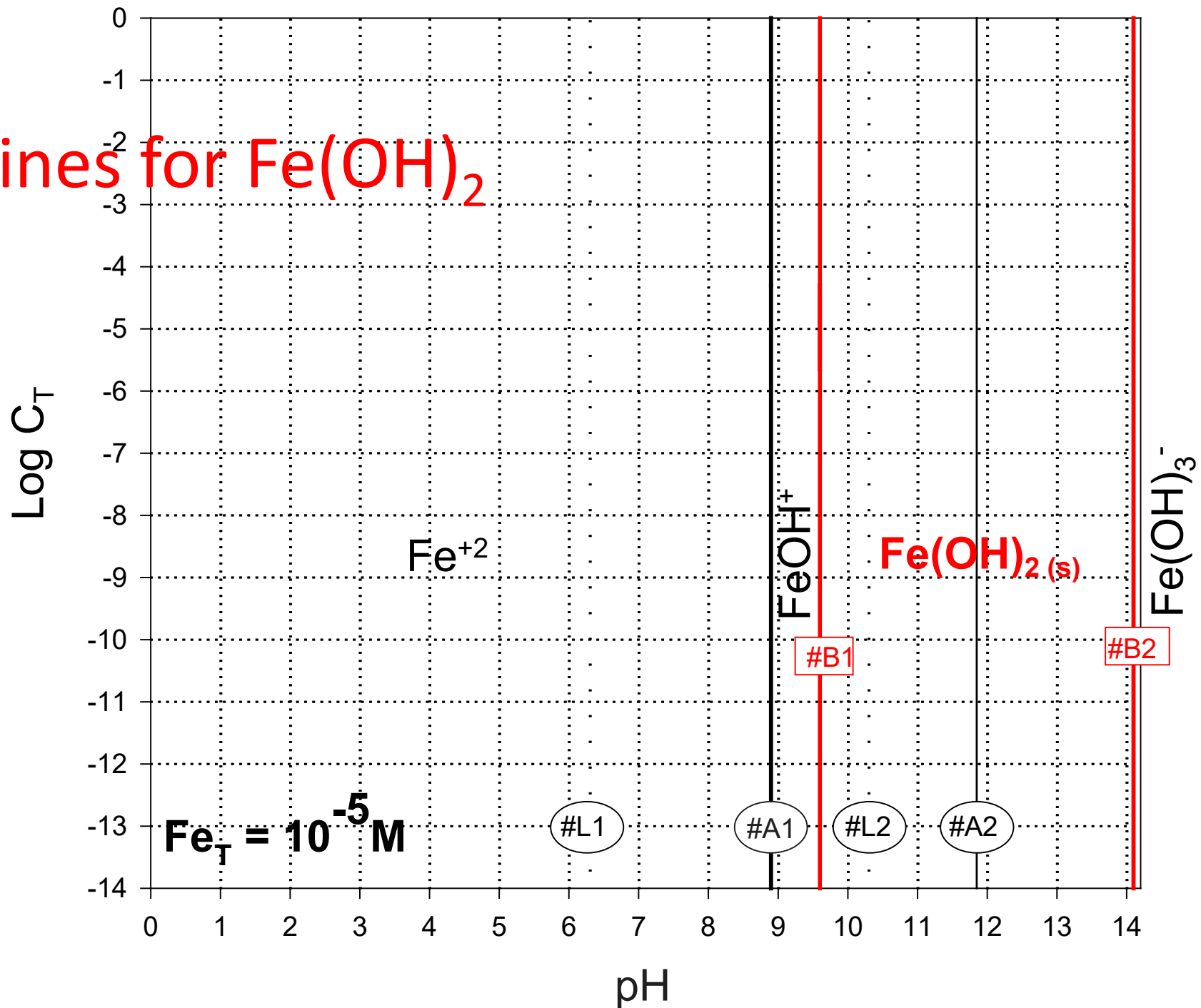
$$pH = 19.1 - 5.0$$

$$pH = 14.1$$

Fe(OH)<sub>3</sub><sup>-</sup> predominates @  
pH > 11.85, so this assumption is  
valid.

**Equation #B2**

# B Lines for $\text{Fe}(\text{OH})_2$



# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example VI

- Type B lines for Fe(CO)<sub>3(s)</sub>
  - Incorporates both a metal (Fe) and a ligand (CO<sub>3</sub>) that undergo pH-dependent speciation
    - Thus there are certain combinations of species that must be considered (the 5 below)
    - and some that never co-exist and therefore don't need to be considered

pH for L	<6.3	6.3-10.3		>10.3	
pH for M	<8.9		8.9-11.85		>11.85
Dominant species	Fe <sup>+2</sup> H <sub>2</sub> CO <sub>3</sub>	Fe <sup>+2</sup> HCO <sub>3</sub> <sup>-</sup>	FeOH <sup>+</sup> HCO <sub>3</sub> <sup>-</sup>	FeOH <sup>+</sup> CO <sub>3</sub> <sup>-2</sup>	Fe(OH) <sub>3</sub> <sup>-</sup> CO <sub>3</sub> <sup>-2</sup>
pH range	<6.3	6.3-8.9	8.9-10.3	10.3-11.85	>11.85
Equ #	B3a	B3b	B4b	B4c	B5c

Soluble Species  
Predominance Table

# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example VII

- Type B lines
  - Fe(CO<sub>3</sub>)<sub>(s)</sub>
    - First look at Fe<sup>+2</sup> and the precipitate at low pH

$$10^{-10.7} = [Fe^{+2}][CO_3^{-2}] = [Fe^{+2}]\alpha_2 C_T$$

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

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

H<sub>2</sub>CO<sub>3</sub> predominates  
@pH < 6.3  
(Assumption #1)

$$10^{-10.7} = [Fe^{+2}]K_1 K_2 [H^+]^{-2} C_T$$

$$C_T = 10^{-10.7} [Fe^{+2}]^{-1} K_1^{-1} K_2^{-1} C_T^{-1} [H^+]^2$$

$$\log C_T = -10.7 + pK_1 + pK_2 - \log[Fe^{+2}] - 2pH$$

$$= 5.9 - \log[Fe^{+2}] - 2pH$$

Fe<sup>+2</sup> predominates @ pH < 8.9, so the 2 assumptions are only valid in that pH range: <6.3

Assumption #2,  
[Fe<sup>+2</sup>] ≈ Fe<sub>T</sub> = 10<sup>-5</sup>,  
Then:

$$\log C_T = 5.9 - \log Fe_T - 2pH$$

$$= 5.9 - (-5) - 2pH$$

**Equation #B3a**

$$\log C_T = 10.9 - 2pH$$

# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example VIII

- Type B lines
  - Fe(CO<sub>3</sub>)<sub>(s)</sub>
    - First look at Fe<sup>+2</sup> and the precipitate at mid pH

$$10^{-10.7} = [Fe^{+2}][CO_3^{-2}] = [Fe^{+2}]\alpha_2 C_T$$

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

$$\approx \frac{1}{\frac{[H^+]}{K_2}} = \frac{K_2}{[H^+]}$$

HCO<sub>3</sub><sup>-</sup> predominates  
@pH=6.3-10.3  
(Assumption #1)

$$10^{-10.7} = [Fe^{+2}]K_2[H^+]^{-1}C_T$$

$$C_T = 10^{-10.7}[Fe^{+2}]^{-1}K_2^{-1}[H^+]$$

$$\log C_T = -10.7 + pK_2 - \log[Fe^{+2}] - pH$$

$$= -0.4 - \log[Fe^{+2}] - pH$$

Fe<sup>+2</sup> predominates @ pH < 8.9, so the 2 assumptions are only valid in the pH range; 6.3-8.9

Assumption #2,  
[Fe<sup>+2</sup>] ≈ Fe<sub>T</sub> = 10<sup>-5</sup>,  
Then:

$$\log C_T = -0.4 - \log Fe_T - pH$$

$$= -0.4 - (-5) - pH$$

**Equation #B3b**

$$\log C_T = 4.6 - pH$$



# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example IX

- So far we've looked at the low and mid range pH for Fe<sup>+2</sup> and the carbonate precipitate (lines B3a and B3b, boxed in table below)
- No need to look at the highest pH range (no B3c), because we know that Fe<sup>+2</sup> and CO<sub>3</sub><sup>-2</sup> don't coexist as dominant species

pH for L	<6.3	6.3-10.3		>10.3	
pH for M	<8.9		8.9-11.85		>11.85
Dominant species	Fe <sup>+2</sup> H <sub>2</sub> CO <sub>3</sub>	Fe <sup>+2</sup> HCO <sub>3</sub> <sup>-</sup>	FeOH <sup>+</sup> HCO <sub>3</sub> <sup>-</sup>	FeOH <sup>+</sup> CO <sub>3</sub> <sup>-2</sup>	Fe(OH) <sub>3</sub> <sup>-</sup> CO <sub>3</sub> <sup>-2</sup>
pH range	<6.3	6.3-8.9	8.9-10.3	10.3-11.85	>11.85
Equ #	B3a	B3b	B4b	B4c	B5c

$$10^{-5.6} = [FeOH^+][CO_3^{2-}]/[OH^-] = [FeOH^+]\alpha_2 C_T / [OH^-]$$

# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example X

- Type B lines
  - Fe(CO<sub>3</sub>)<sub>(s)</sub>
    - Next look at FeOH<sup>+</sup> and the precipitate at mid pH

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

$$\approx \frac{1}{\frac{[H^+]}{K_2}} = \frac{K_2}{[H^+]}$$

HCO<sub>3</sub><sup>-</sup> predominates  
@pH=6.3-10.3  
(Assumption #1)

$$10^{-5.6} = [FeOH^+] K_2 [H^+]^{-1} C_T [OH^-]^{-1}$$

$$C_T = 10^{-5.6} [FeOH^+]^{-1} K_2^{-1} [H^+] [OH^-]$$

$$= 10^{-5.6} [FeOH^+]^{-1} K_2^{-1} K_w$$

$$\log C_T = -5.6 - pK_w + pK_2 - \log [FeOH^+]$$

$$= -9.3 - \log [FeOH^+]$$

FeOH<sup>+</sup> predominates @  
pH=8.9-11.85, so the 2  
assumptions are only valid in  
the pH range; 8.9-10.3

Assumption #2,  
[FeOH<sup>+</sup>] ≈ Fe<sub>T</sub> = 10<sup>-5</sup>,  
Then:

$$\log C_T = -9.3 - \log Fe_T$$

$$= -9.3 - (-5)$$

**Equation #B4b**

$$\log C_T = -4.3$$

$$10^{-5.6} = [FeOH^+][CO_3^{2-}]/[OH^-] = [FeOH^+]\alpha_2 C_T / [OH^-]$$

# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example XI

- Type B lines
  - Fe(CO<sub>3</sub>)<sub>(s)</sub>
    - Next look at FeOH<sup>+</sup> and the precipitate at high pH

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

$$\approx 1$$

CO<sub>3</sub><sup>2-</sup> predominates  
@pH>10.3  
(Assumption #1)

$$10^{-5.6} = [FeOH^+] C_T [OH^-]^{-1}$$

$$C_T = 10^{-5.6} [FeOH^+]^{-1} [OH^-]$$

$$= 10^{-5.6} [FeOH^+]^{-1} K_w [H^+]^{-1}$$

$$\log C_T = -5.6 - pK_w - \log [FeOH^+] + pH$$

$$= -19.6 - \log [FeOH^+] + pH$$

FeOH<sup>+</sup> predominates @  
pH=8.9-11.85, so the 2  
assumptions are only valid in  
the pH range; 10.3-11.85

Assumption #2,  
[FeOH<sup>+</sup>] ≈ Fe<sub>T</sub> = 10<sup>-5</sup>,  
Then:

$$\log C_T = -19.6 - \log Fe_T + pH$$

$$= -19.6 - (-5) + pH$$

**Equation #B4c**

$$\log C_T = -14.6 + pH$$

# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example XII

- At this point we've looked at the 2 relevant pH ranges for Fe<sup>+2</sup> or Fe(OH)<sup>+</sup> and the carbonate precipitate (lines B3a,B3b,B4b and B4c, boxed in table below)
- No need to look at the lowest pH range for FeOH<sup>+</sup>, and we only need to look at the highest pH range for Fe(OH)<sub>3</sub><sup>-</sup> (no B3c, B5a, B5b)

pH for L	<6.3	6.3-10.3		>10.3	
pH for M	<8.9		8.9-11.85		>11.85
Dominant species	Fe <sup>+2</sup> H <sub>2</sub> CO <sub>3</sub>	Fe <sup>+2</sup> HCO <sub>3</sub> <sup>-</sup>	FeOH <sup>+</sup> HCO <sub>3</sub> <sup>-</sup>	FeOH <sup>+</sup> CO <sub>3</sub> <sup>-2</sup>	Fe(OH) <sub>3</sub> <sup>-</sup> CO <sub>3</sub> <sup>-2</sup>
pH range	<6.3	6.3-8.9	8.9-10.3	10.3-11.85	>11.85
Equ #	B3a	B3b	B4b	B4c	B5c

$$10^{-1.3} = [Fe(OH)_3^-][CO_3^{2-}]/[OH^-]^3 = [Fe(OH)_3^-]\alpha_2 C_T / [OH^-]^3$$

# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example XIII

- Type B lines
  - Fe(CO<sub>3</sub>)<sub>(s)</sub>
    - Finally look at Fe(OH)<sub>3</sub><sup>-</sup> and the precipitate at high pH

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

CO<sub>3</sub><sup>2-</sup> predominates @pH>10.3 (Assumption #1)

$$10^{-1.3} = [Fe(OH)_3^-] C_T [OH^-]^{-1}$$

$$C_T = 10^{-1.3} [Fe(OH)_3^-]^{-1} [OH^-]^3$$

$$= 10^{-1.3} [Fe(OH)_3^-]^{-1} K_w^3 [H^+]^{-3}$$

$$\log C_T = -1.3 - 3 pK_w - \log [Fe(OH)_3^-] + 3 pH$$

$$= -43.3 - \log [Fe(OH)_3^-] + 3 pH$$

Fe(OH)<sub>3</sub><sup>-</sup> predominates @ pH>11.85, so the 2 assumptions are only valid in the pH range; >11.85

Assumption #2, [Fe(OH)<sub>3</sub><sup>+</sup>] ≈ Fe<sub>T</sub> = 10<sup>-5</sup>, Then:

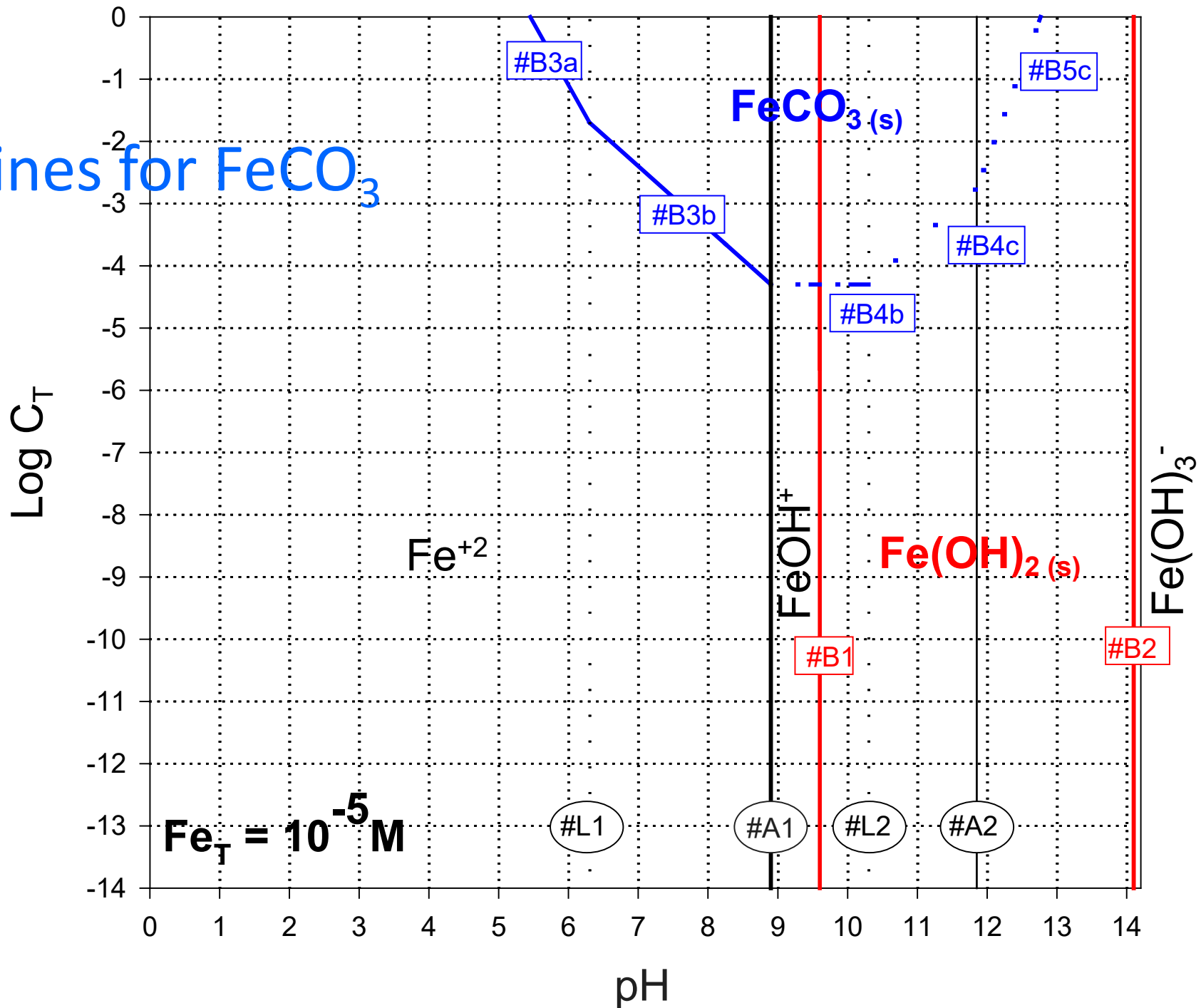
$$\log C_T = -43.4 - \text{Log} Fe_T + 3 pH$$

$$= -43.3 - (-5) + 3 pH$$

**Equation #B5c**

$$\log C_T = -38.3 + 3 pH$$

# B Lines for $\text{FeCO}_3$



# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example XIV

- Type C lines: concern interface between two different precipitates
  - FeOH<sub>(s)</sub> and Fe(CO<sub>3</sub>)<sub>(s)</sub>
    - First look at Fe<sup>+2</sup> and the precipitate

Fe(OH)<sub>2(s)</sub> K<sub>so</sub>

$$10^{-14.5} = [Fe^{+2}][OH^{-}]^2$$

$$[Fe^{+2}] = 10^{-14.5} [OH^{-}]^{-2} = 10^{-14.5} K_w^{-2} [H^{+}]^2$$

$$= 10^{+13.5} [H^{+}]^2$$

FeCO<sub>3(s)</sub> K<sub>so</sub>

$$10^{-10.7} = [Fe^{+2}][CO_3^{-2}]$$

$$[CO_3^{-2}] = 10^{-10.7} [Fe^{+2}]^{-1}$$

Use for the C1 lines

$$[CO_3^{-2}] = 10^{-10.7} 10^{-13.5} [H^{+}]^{-2}$$

$$\alpha_2 C_T = 10^{-24.2} [H^{+}]^{-2}$$

$$\log C_T = -\log \alpha_2 - 24.2 + 2pH$$

$$\log C_T = -\log \alpha_2 - 24.2 + 2pH$$

# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example XV

- Type C lines
  - FeOH<sub>(s)</sub> and Fe(CO<sub>3</sub>)<sub>(s)</sub>
    - Both phases exist
      - Assumption #1
    - First look at low pH

$$\alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1}$$

$$\approx \frac{1}{\frac{[H^+]^2}{K_1K_2}} = \frac{K_1K_2}{[H^+]^2}$$

H<sub>2</sub>CO<sub>3</sub> predominates  
@pH<6.3  
(Assumption #2)

$$\log C_T = -\log(K_1K_2/[H^+]^2) - 24.2 + 2pH$$

$$= pK_1 + pK_2 - 24.2$$

$$\log C_T = -7.6$$

H<sub>2</sub>CO<sub>3</sub> predominates @ pH<6.3, so assumption #1 is only valid in that pH range: <6.3. This may be further restricted by assumption #1, which can be evaluated when plotting.

**Equation #C1a**



# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example XVI

## • Type C lines

- FeOH<sub>(s)</sub> and Fe(CO<sub>3</sub>)<sub>(s)</sub>
  - Both phases exist
    - Assumption #1
  - Next look at mid pH

HCO<sub>3</sub><sup>-</sup> predominates @ pH=6.3-10.3, so assumption #1 is only valid in that pH range: 6.3-10.3. This may be further restricted by assumption #1, which can be evaluated when plotting.

$$\log C_T = -\log \alpha_2 - 24.2 + 2pH$$

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

$$\approx \frac{1}{\frac{[H^+]}{K_2}} = \frac{K_2}{[H^+]}$$

HCO<sub>3</sub><sup>-</sup> predominates  
@pH=6.3-10.3  
(Assumption #2)

$$\log C_T = -\log(K_2/[H^+]) - 24.2 + 2pH$$

$$= pK_2 - 24.2 + pH$$

$$\log C_T = -13.9 + pH$$

**Equation #C1b**

# Fe(OH)<sub>2</sub> & FeCO<sub>3</sub> example XVII

## • Type C lines

- FeOH<sub>(s)</sub> and Fe(CO<sub>3</sub>)<sub>(s)</sub>
  - Both phases exist
    - Assumption #1
  - Lastly look at high pH

CO<sub>3</sub><sup>-2</sup> predominates @ pH>10.3, so assumption #1 is only valid in that pH range: >10.3. This may be further restricted by assumption #1, which can be evaluated when plotting.

$$\log C_T = -\log \alpha_2 - 24.2 + 2pH$$

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

≈ 1

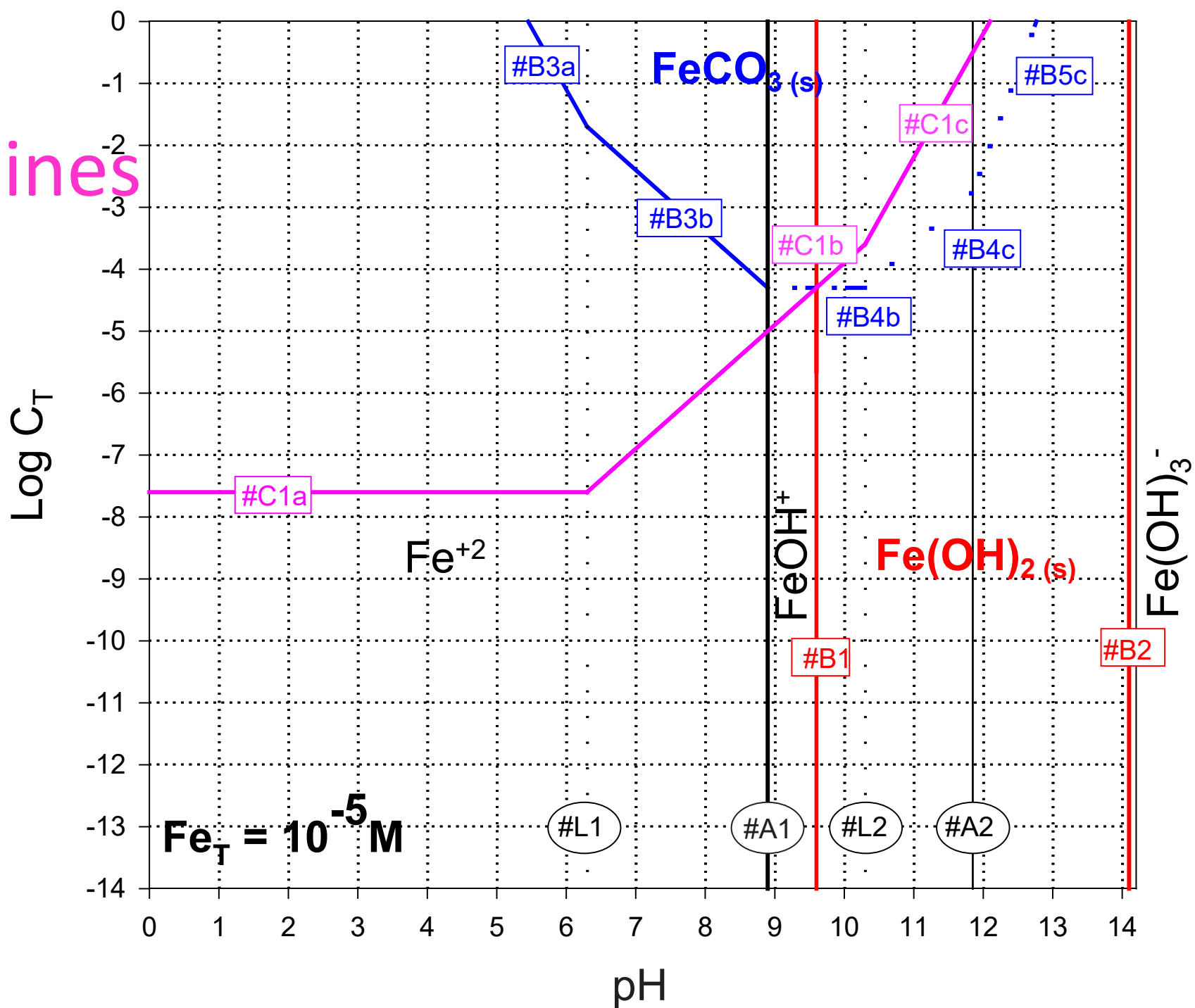
CO<sub>3</sub><sup>-2</sup> predominates  
@pH>10.3  
(Assumption #2)

$$\log C_T = -\log(1) - 24.2 + 2pH$$

$$\log C_T = -24.2 + 2pH$$

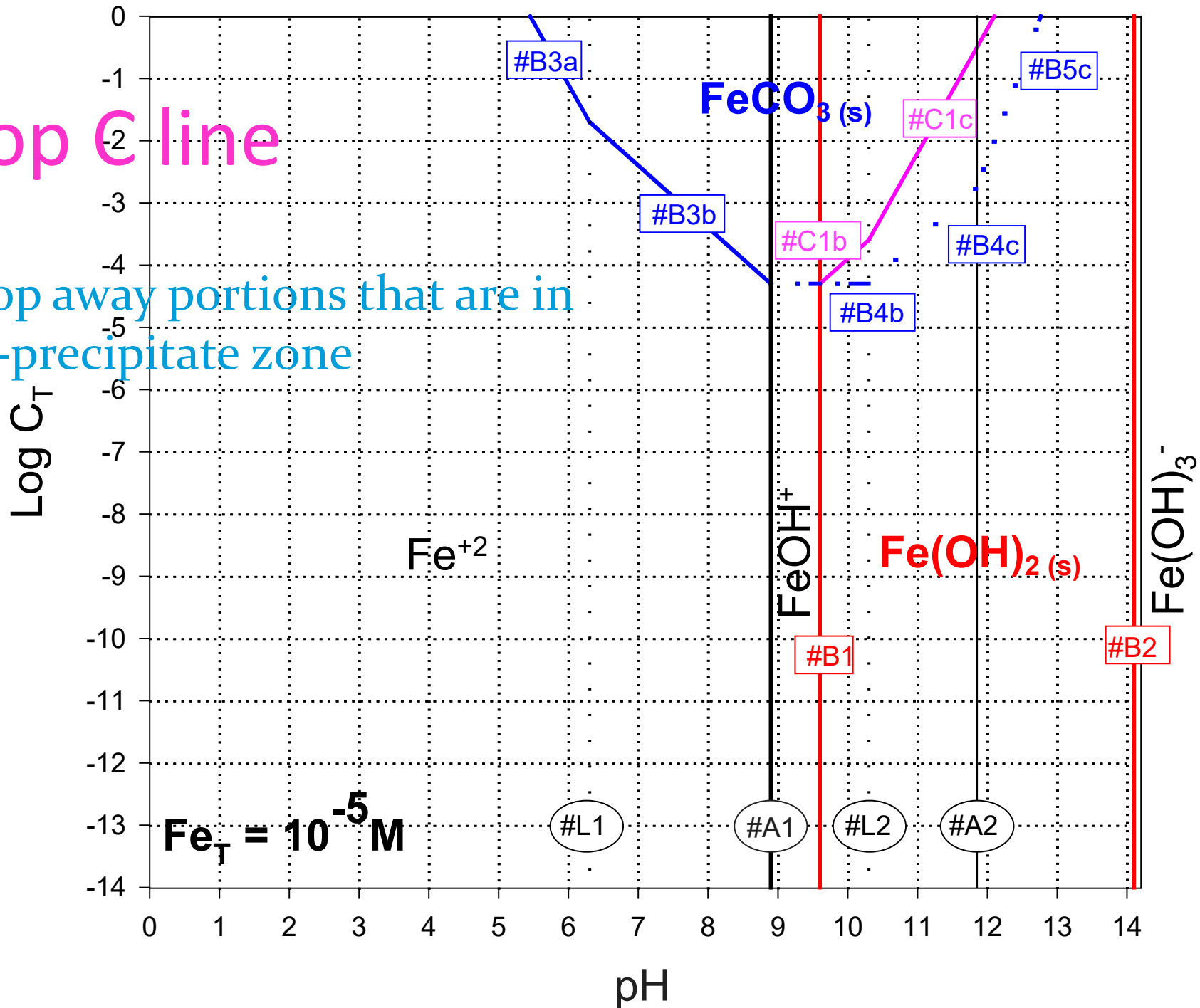
**Equation #C1c**

# C lines



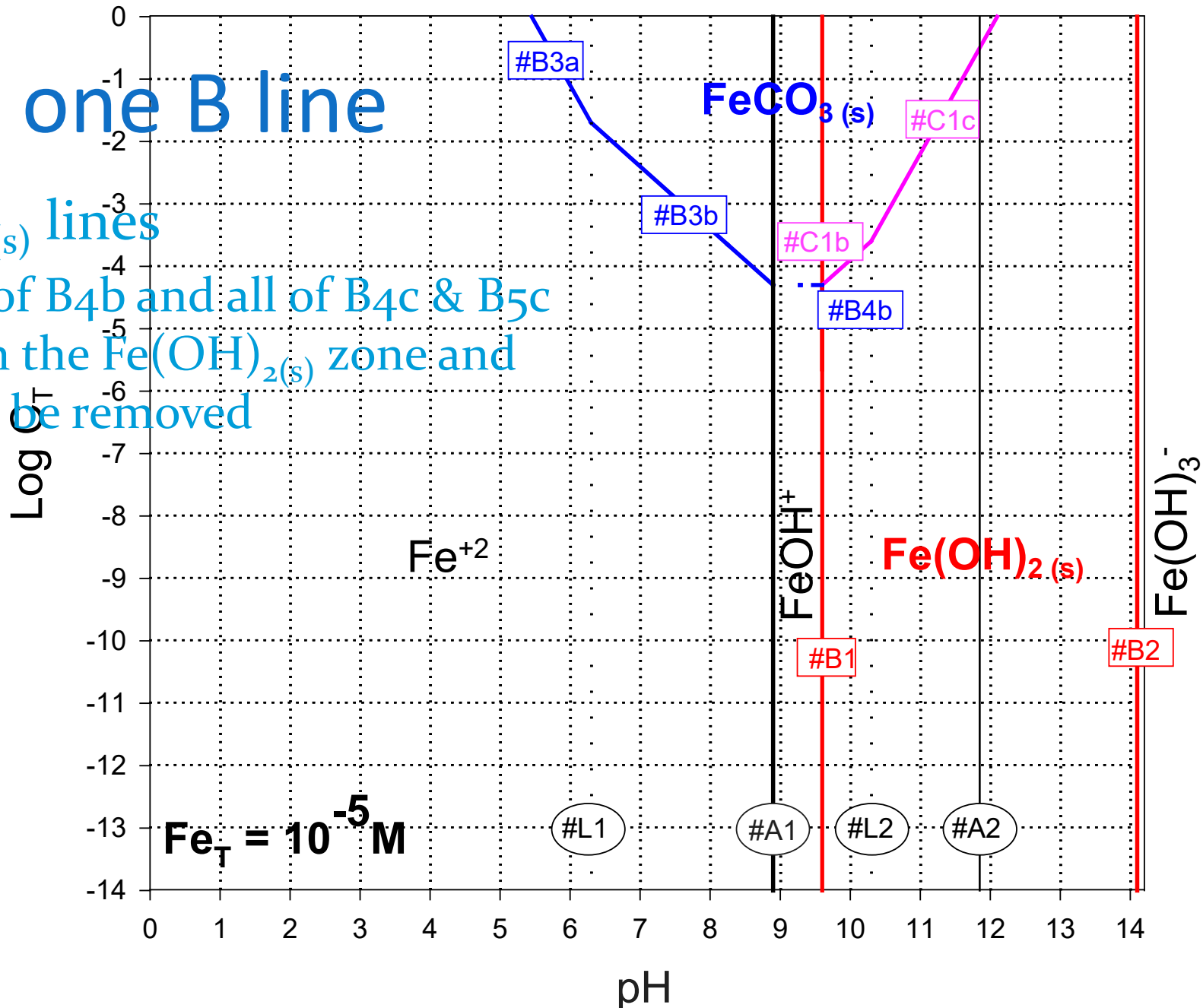
# Crop C line

- Crop away portions that are in no-precipitate zone



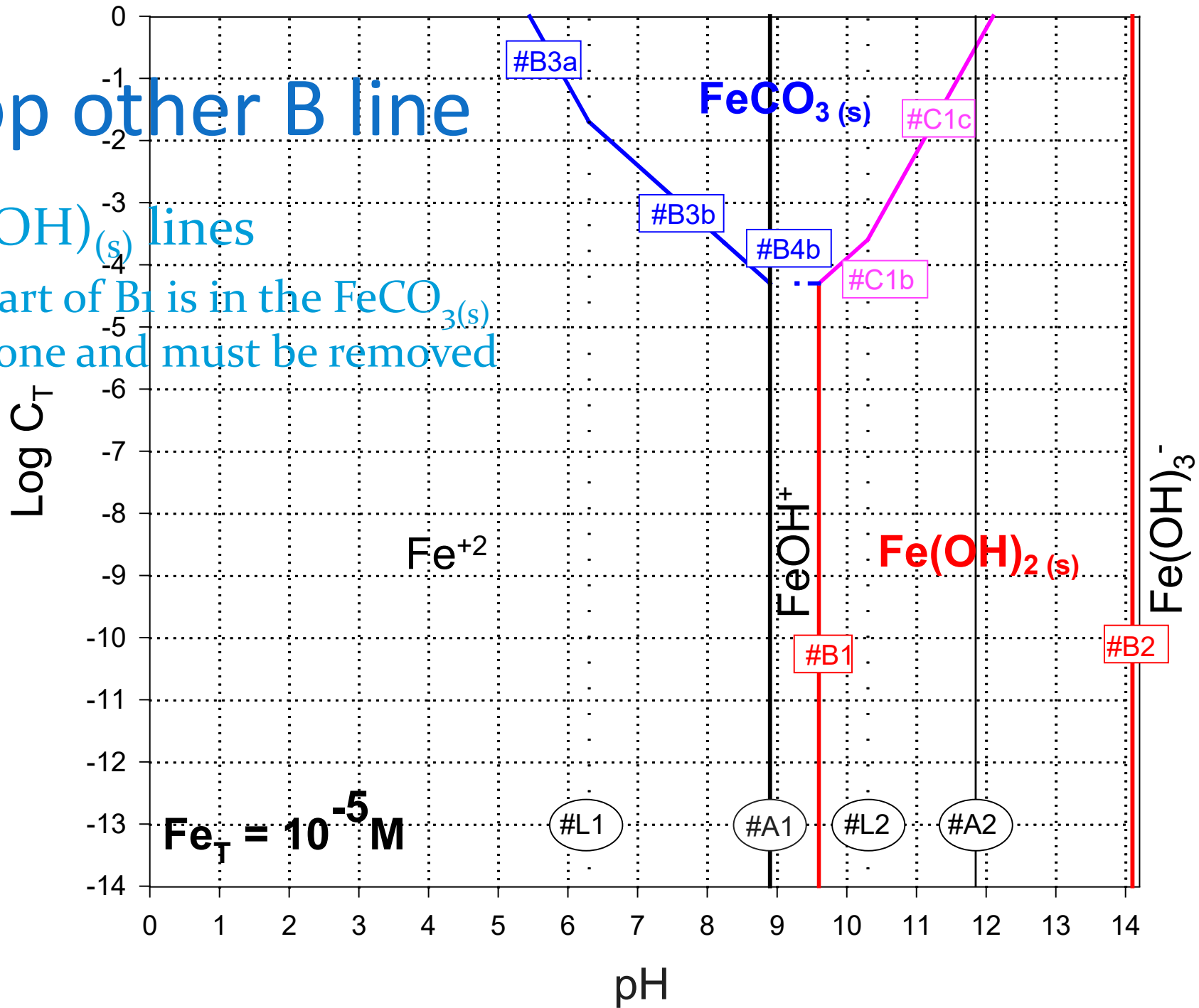
# Crop one B line

- $\text{FeCO}_3(s)$  lines
  - Part of B4b and all of B4c & B5c are in the  $\text{Fe}(\text{OH})_2(s)$  zone and must be removed



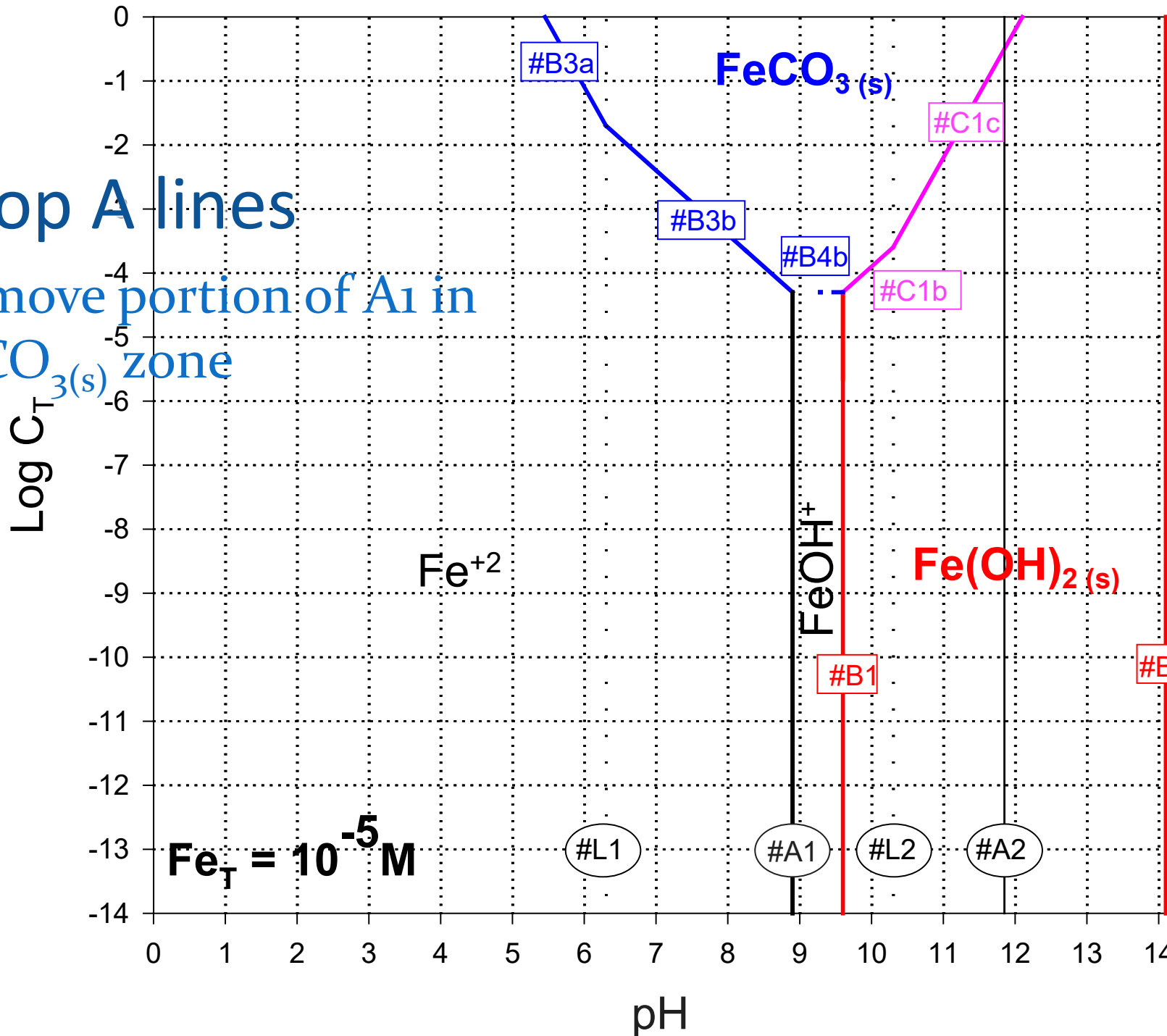
# Crop other B line

- $\text{Fe}(\text{OH})_3(\text{s})$  lines
- Part of B1 is in the  $\text{FeCO}_3(\text{s})$  zone and must be removed

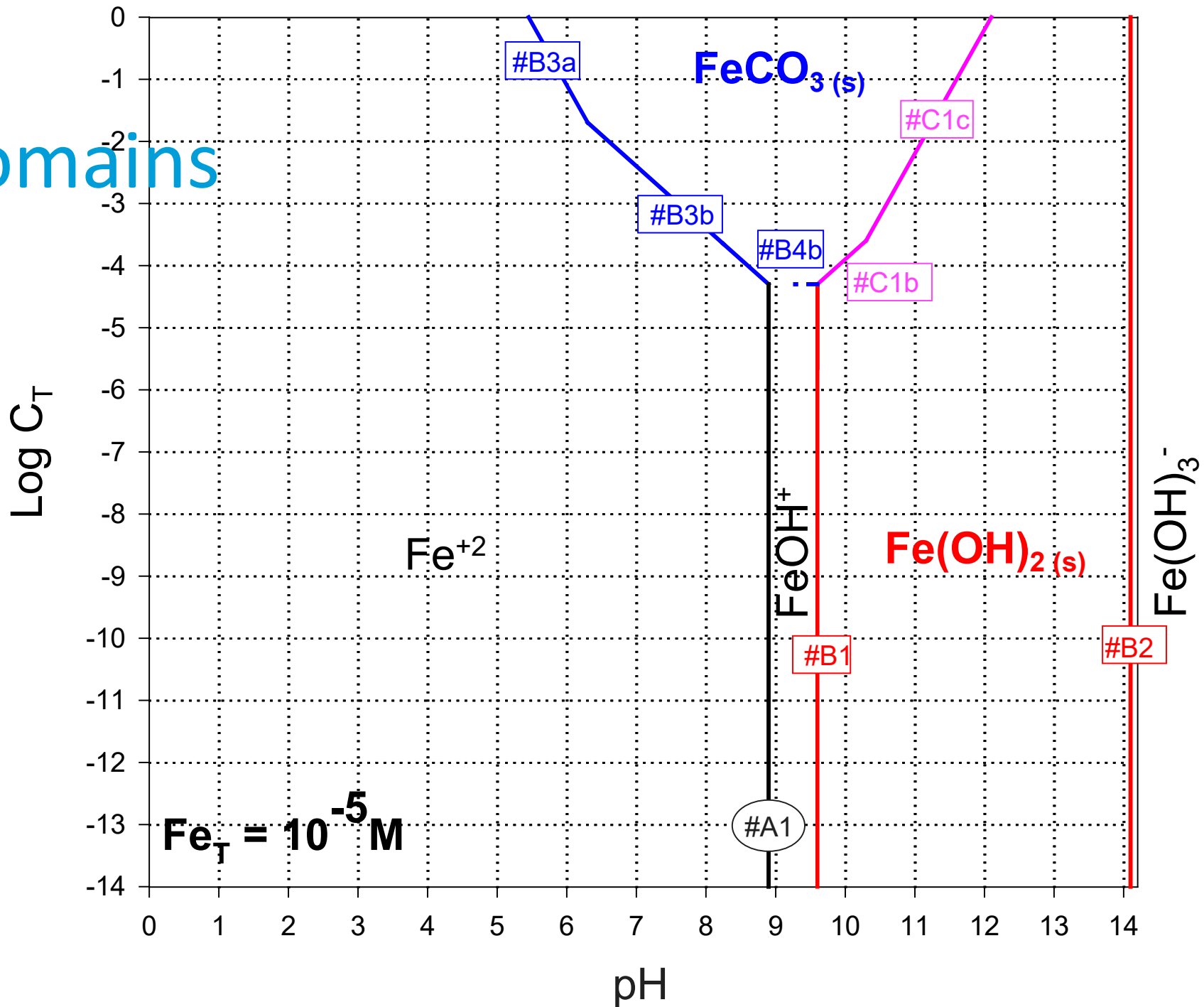


# Crop A lines

- Remove portion of A1 in  $\text{FeCO}_3(s)$  zone

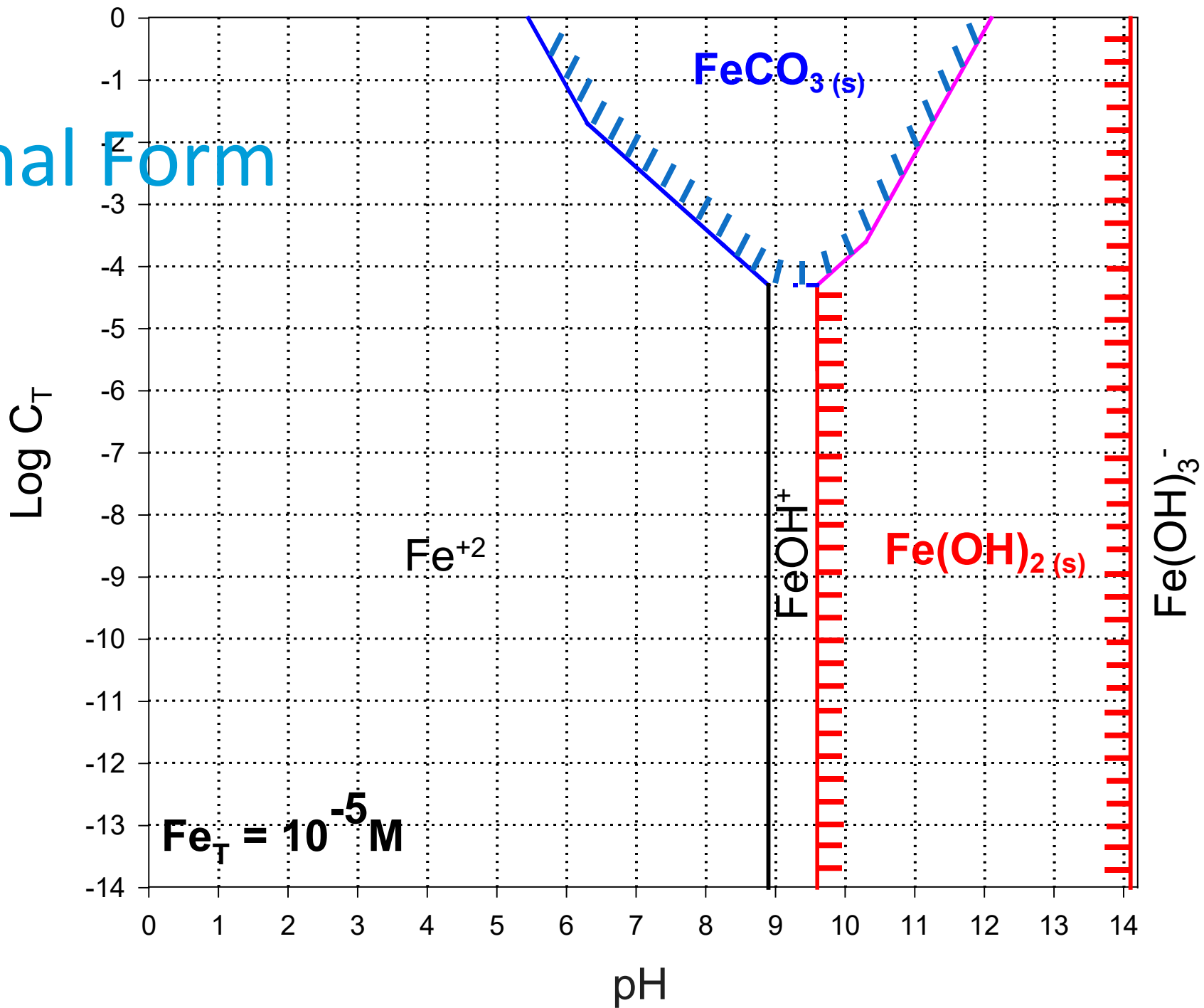


# Domains





# Final Form

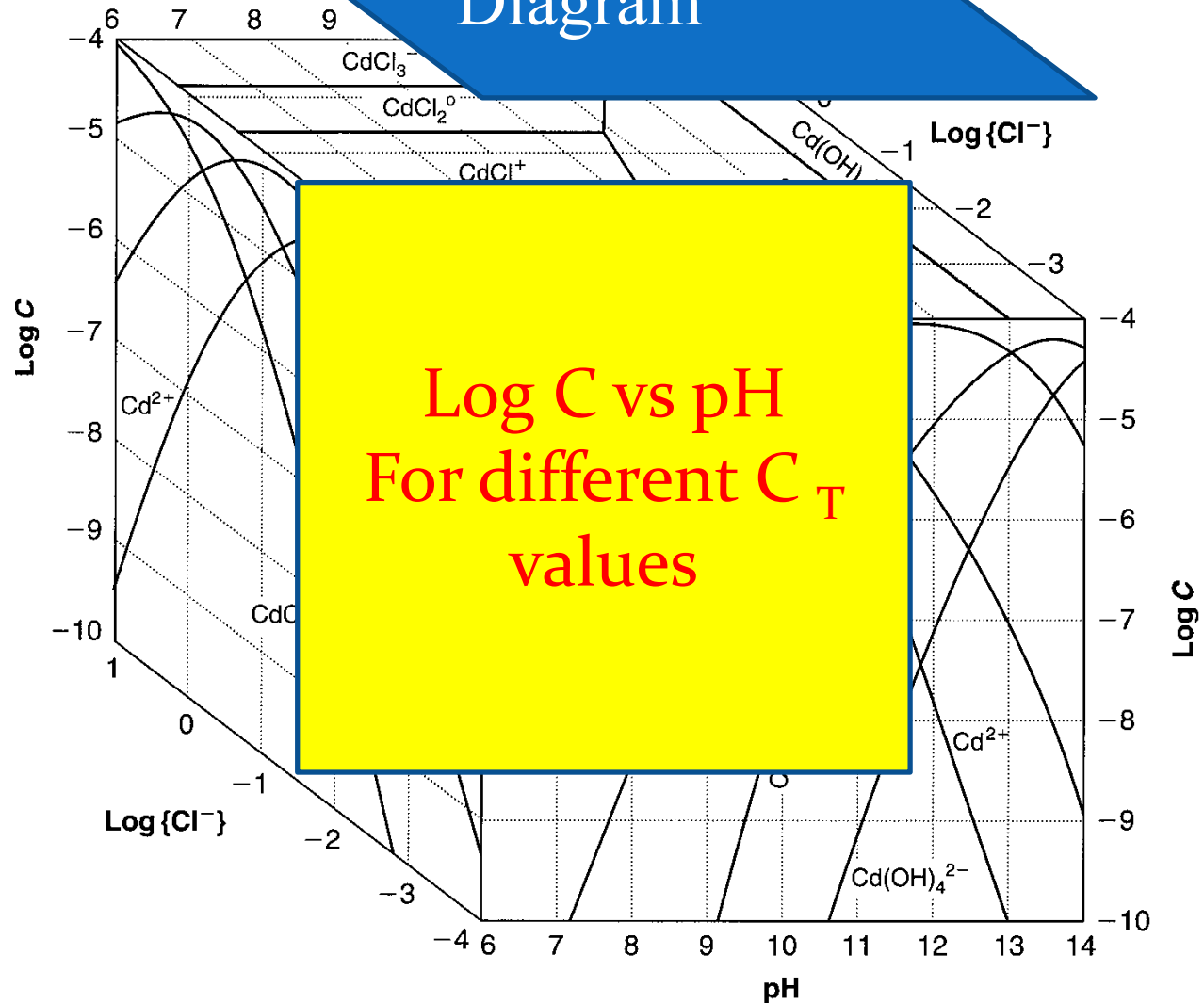


# 3-D form

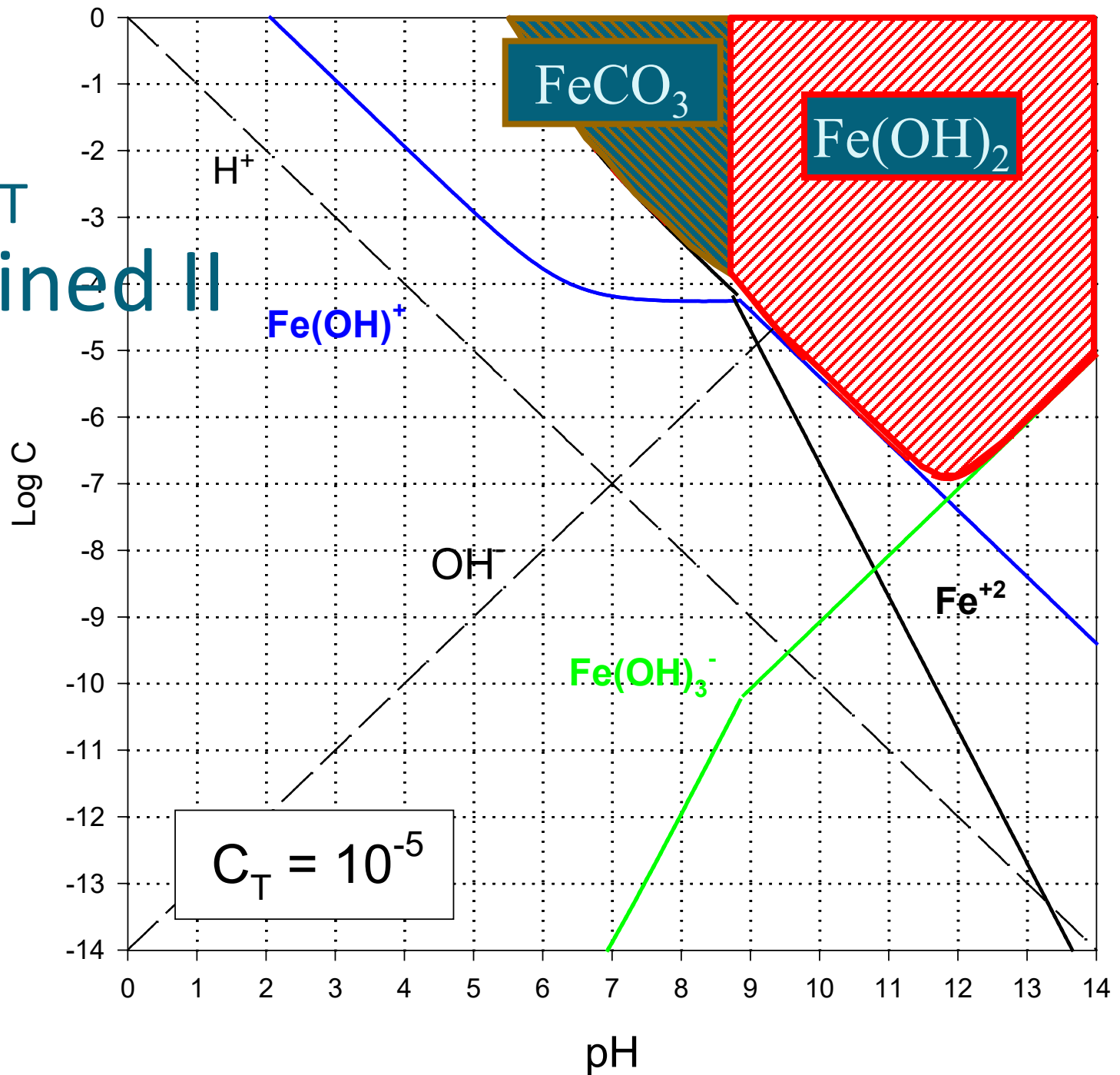
## Predominance Diagram

Fig. 2.7 in  
Benjamin

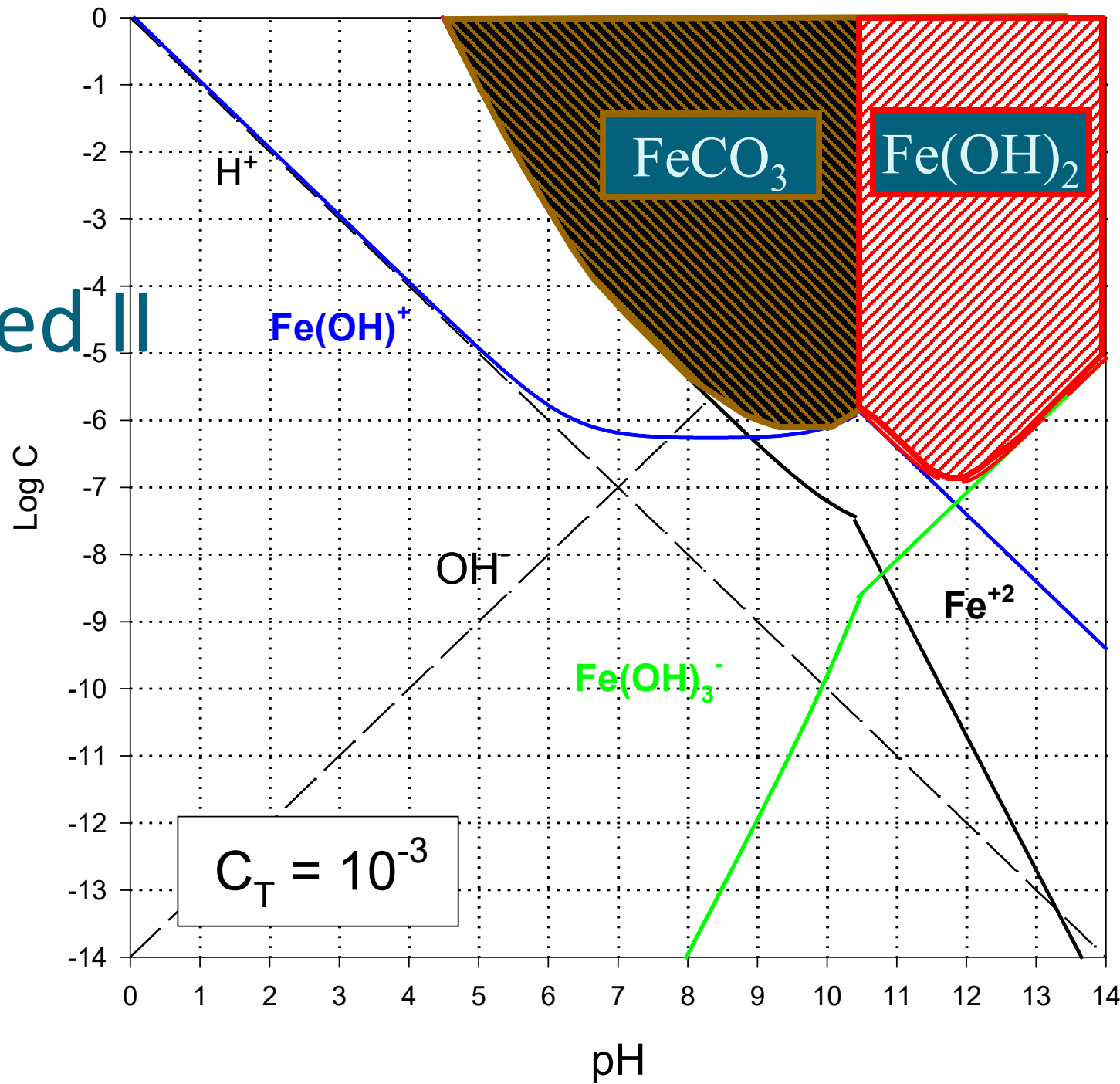
Log C  
vs  
Log C<sub>T</sub>



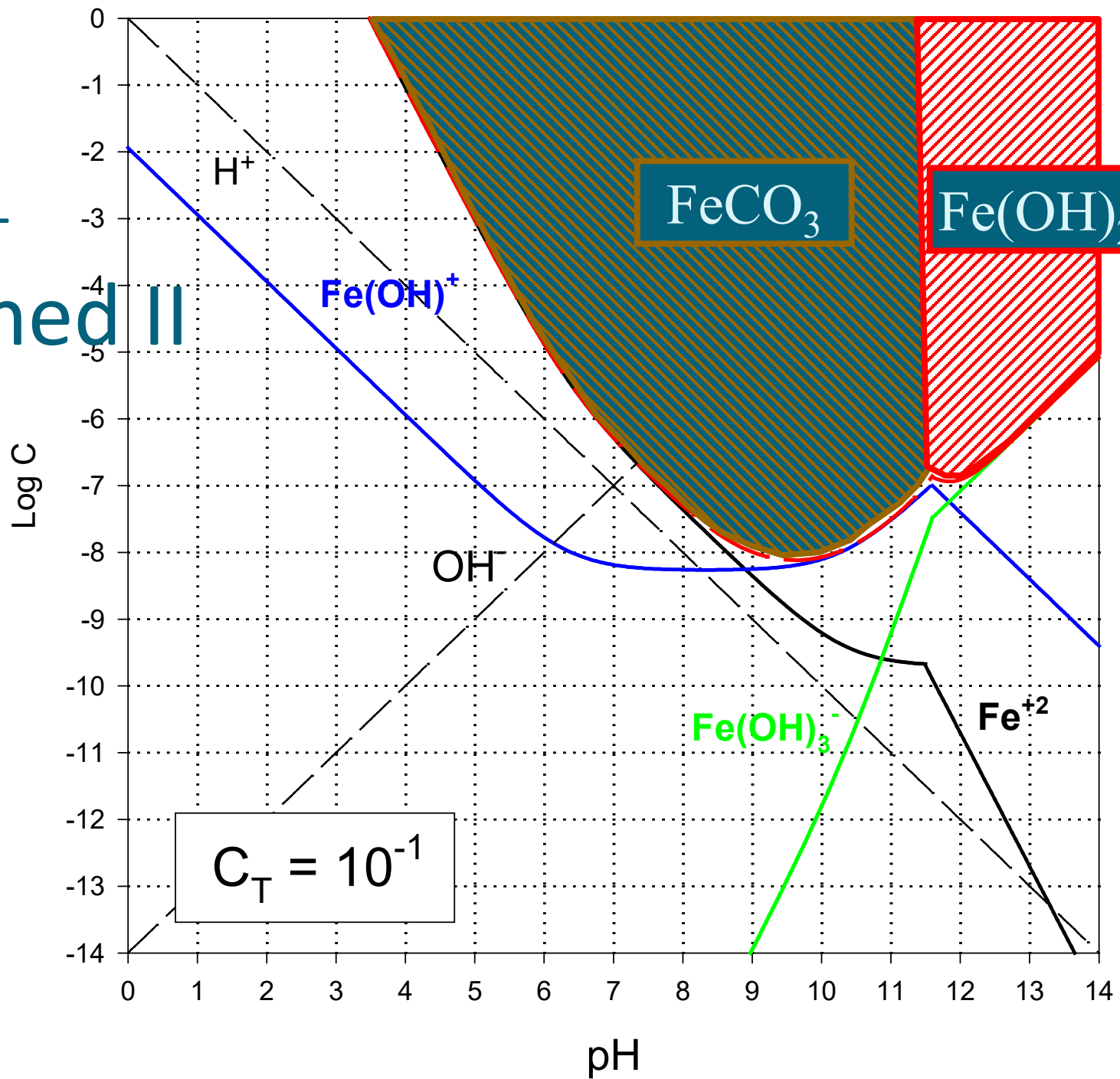
# Low $C_T$ Combined II



# Mid $C_T$ Combined II

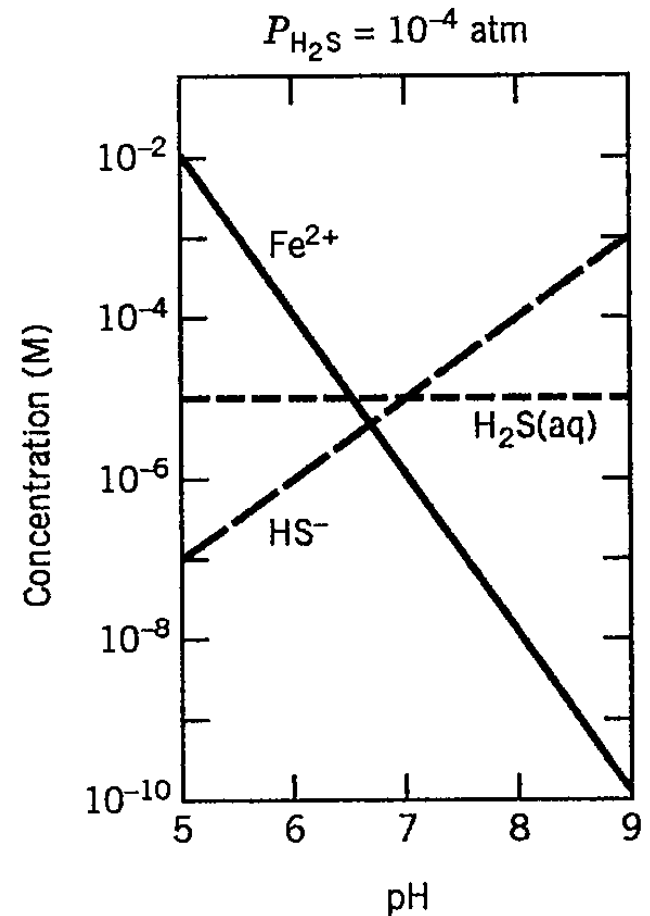


# High $C_T$ Combined II



# Ferrous Sulfide

Stumm &  
Morgan, 1996,  
Figure 7.17, pg.  
401



**Table 7.4. Solubility of Sulfides (25°C, I = 0)<sup>a</sup>**

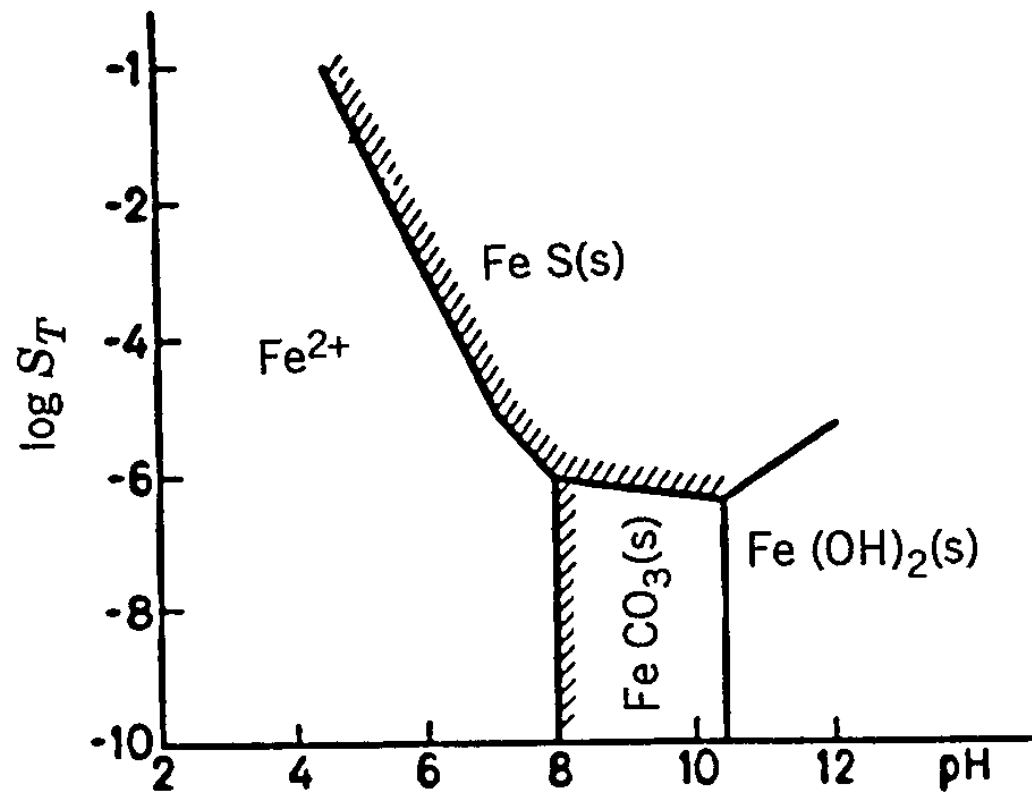
		$\text{MeS(s)} + \text{H}^+ = \text{Me}^{2+} + \text{HS}^-$	$*K_s = K_{s0}K_2^{-1}$
		$\text{M}_2\text{S(s)} + \text{H}^+ = 2 \text{M}^+ + \text{HS}^-$	$*K_s = K_{s0}K_2^{-1}$
Sulfide		log $*K_s$	Reference
MnS	(green)	0.17	Dyrssen and Kremling (1990)
	(pink)	3.34	Dyrssen and Kremling (1990)
FeS		-4.2	Dyrssen and Kremling (1990)
	(troilite)	-5.25	Davison (1991)
	(mackinawite)	-3.6	Davison (1991)
	(amorphous)	-2.95	Davison (1991)
	(pyrrhotite)	-5.1	Davison (1991)
Fe <sub>3</sub> S <sub>4</sub>	(greigite) <sup>b</sup>	-4.4	Davison (1991)
FeS <sub>2</sub>	(pyrite) <sup>c</sup>	-16.4	Davison (1991)
CoS	(α)	-7.44	Dyrssen and Kremling (1990)
	(β)	-11.07	Dyrssen and Kremling (1990)
NiS	(α)	-5.6	Dyrssen and Kremling (1990)
	(β)	-11.1	Dyrssen and Kremling (1990)
	(γ)	-12.8	Dyrssen and Kremling (1990)
CuS		22.3	Dyrssen and Kremling (1990)
ZnS	(α, sphaalerite)	-10.93	Dyrssen and Kremling (1990)
	(β, wurtzite)	-8.95	Dyrssen and Kremling (1990)
CdS	(greenockite)	-14.36	Daskalakis and Helz (1992)
HgS	(black)	-38.8	Dyrssen and Kremling (1990)
	(red)	-39.5	Dyrssen and Kremling (1990)
SnS		-11.95	Dyrssen and Kremling (1990)
PbS		-13.97	Dyrssen and Kremling (1990)
Cu <sub>2</sub> S		-34.65	Dyrssen and Kremling (1990)
Ag <sub>2</sub> S		-35.94	Dyrssen and Kremling (1990)
Tl <sub>2</sub> S		-7.22	Dyrssen and Kremling (1990)

<sup>a</sup>Where necessary, values of  $K_{s0}$  were converted into  $*K_s$  by assuming  $K_2 = 10^{-13.9}$ .

<sup>b</sup>The solubility equilibrium is defined by  $\text{Fe}_3\text{S}_4(\text{s}) + 3 \text{H}^+ = 3 \text{Fe}^{2+} + 3 \text{HS}^- + \text{S}^0$ ;  $(*K_s)^3$ .

<sup>c</sup>For the equilibrium  $\text{FeS}_2(\text{s}) + \text{H}^+ = \text{Fe}^{2+} + \text{HS}^- + \text{S}^0$ .

Stumm &  
Morgan, 1996,  
Figure 7.18, pg.  
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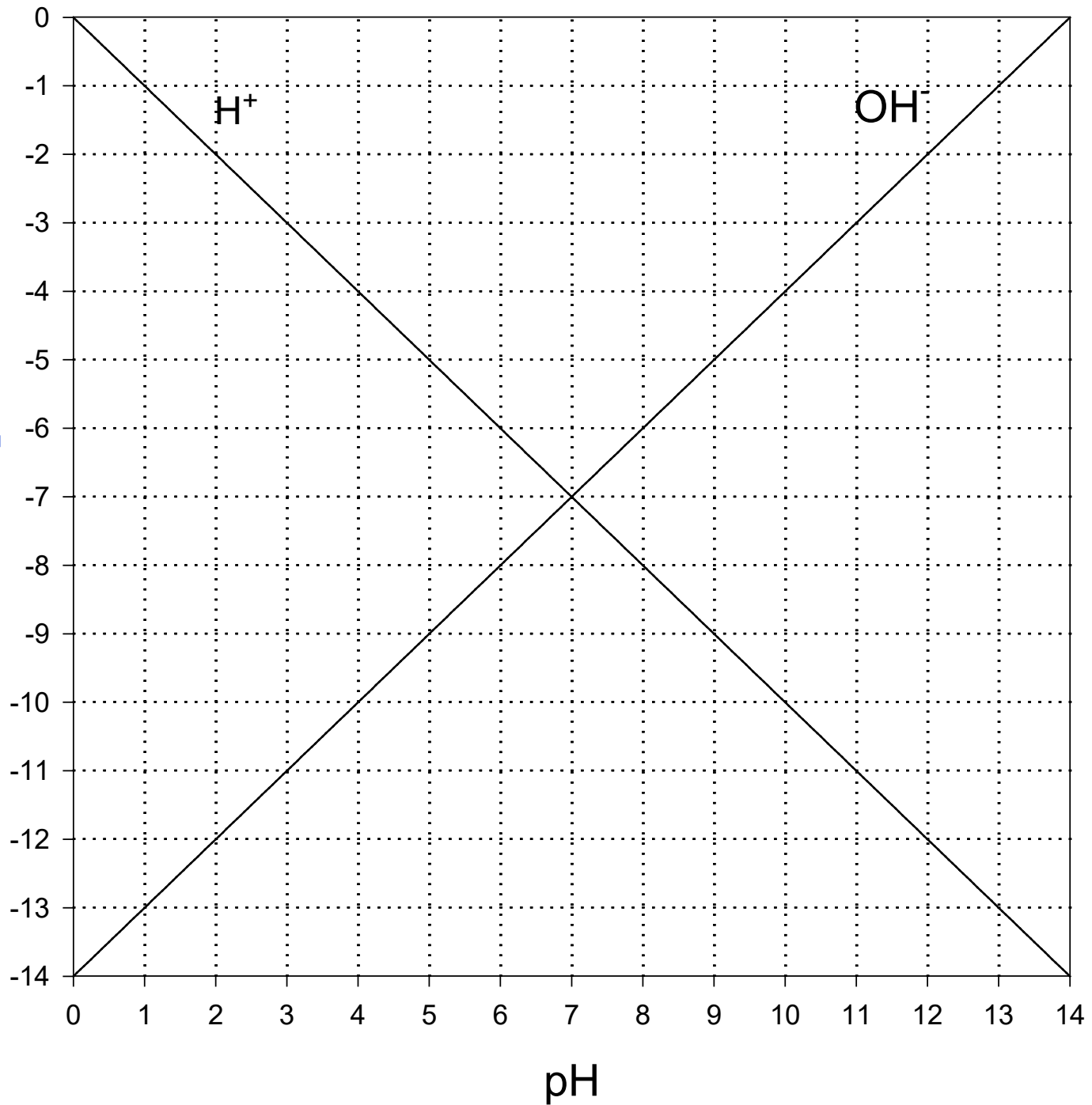






- To next lecture

Log Ct



Log P<sub>CO2</sub>

