Updated: 10 April 2020

Print version

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.

- $Fe(OH)_2(s) = Fe^{+2} + 2OH^-$ $10^{-14.5}$
- $Fe(OH)_2(s) = Fe(OH)^+ + OH^-$ $10^{-9.4}$
- $Fe(OH)_2(s) + OH^- = Fe(OH)_3^-$ $10^{-5.1}$

- $FeCO_3(s) = Fe^{+2} + CO_3^-$ $10^{-10.7}$
- $FeCO_3(s) + OH^- = Fe(OH)^+ + CO_3^{-2}$ $10^{-5.6}$
- $FeCO_3(s) + 3OH^- = Fe(OH)_3^- + CO_3^{-2}$ $10^{-1.3}$

Ferrous Hydroxide/Carbonate Equ.

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

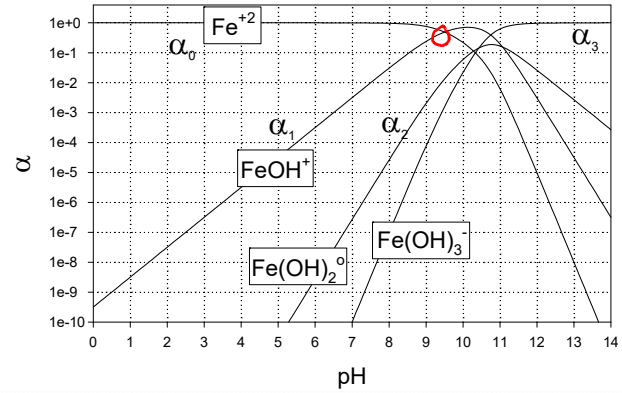
$$\frac{Fe^{+2} + 2OH^-}{Fe(OH)^+ + OH^-} = \frac{10^{-14.5}}{10^{-9.4}} = 10^{-5.1}$$

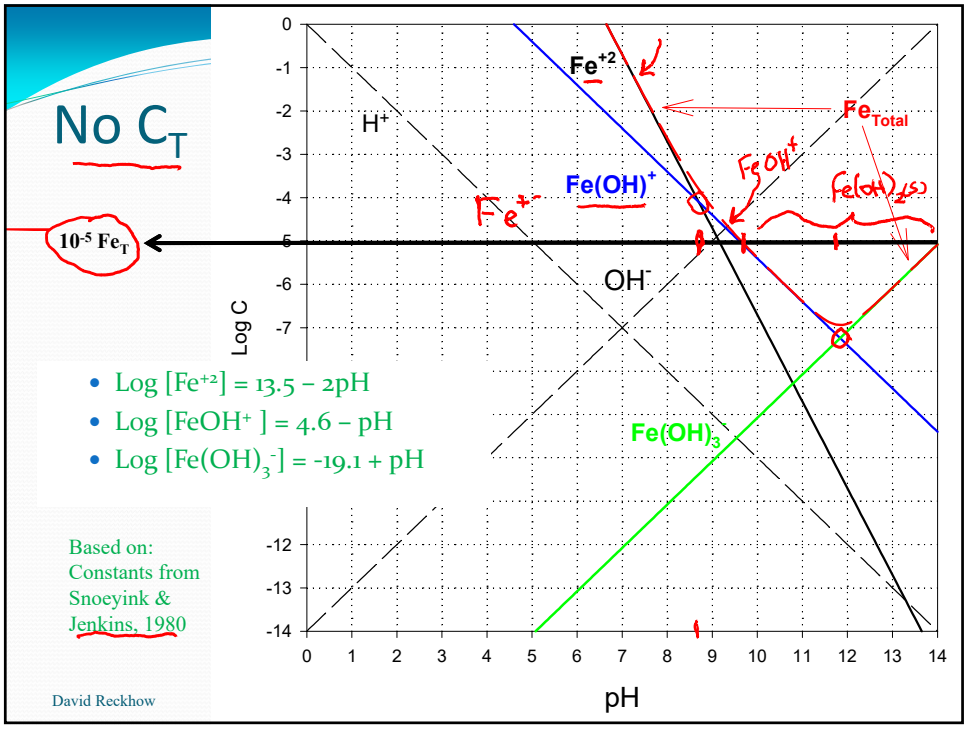
$$1 = \frac{[Fe^{+2}]}{[Fe(OH)^+][H^+]} = 10^{+8.9}$$

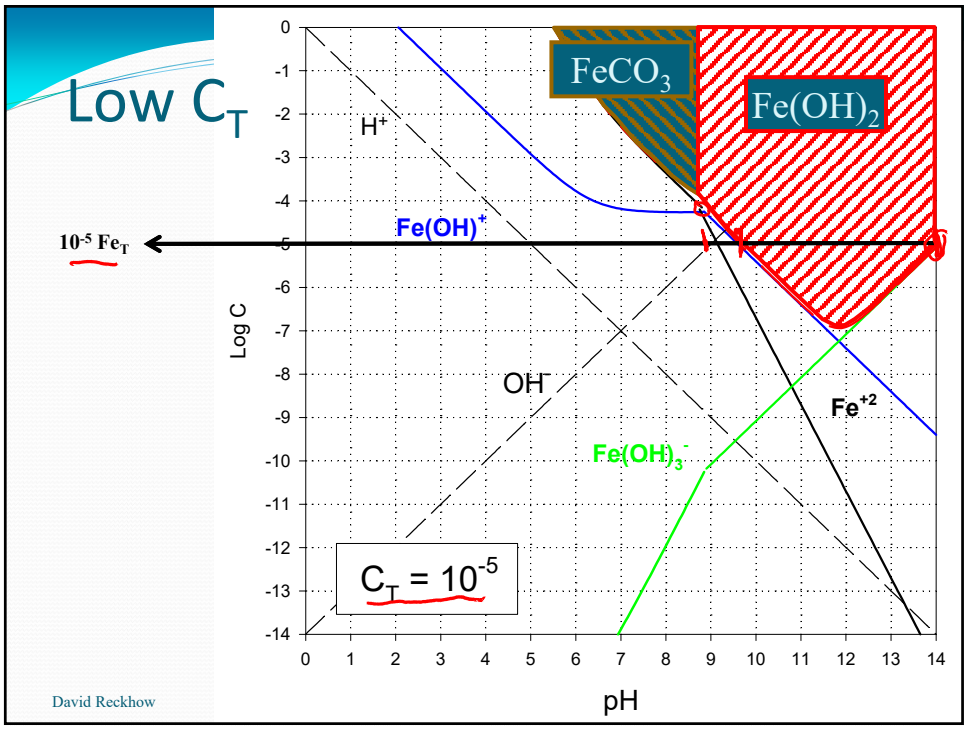
$10^{-8.9}$ pH = 8.9

Ferrous Hydroxides: α diagram

- Soluble predominance diagram




No C_T
10^{-5} Fe_T
Fe^{+2}
H^+
$Fe(OH)^+$
Fe_{Total}
$FeOH^+$
$Fe(OH)_2(s)$
OH^-
$Fe(OH)_3^-$
Log C
pH
• Log [Fe^{+2}] = 13.5 – 2pH
• Log [$FeOH^+$] = 4.6 – pH
• Log [$Fe(OH)_3^-$] = -19.1 + pH
Based on: Constants from Snoeyink & Jenkins, 1980
David Reckhow


Low C_T
10^{-5} Fe_T
$FeCO_3$
$Fe(OH)_2$
H^+
$Fe(OH)^+$
OH^-
Fe^{+2}
$Fe(OH)_3^-$
$C_T = 10^{-5}$
Log C
pH
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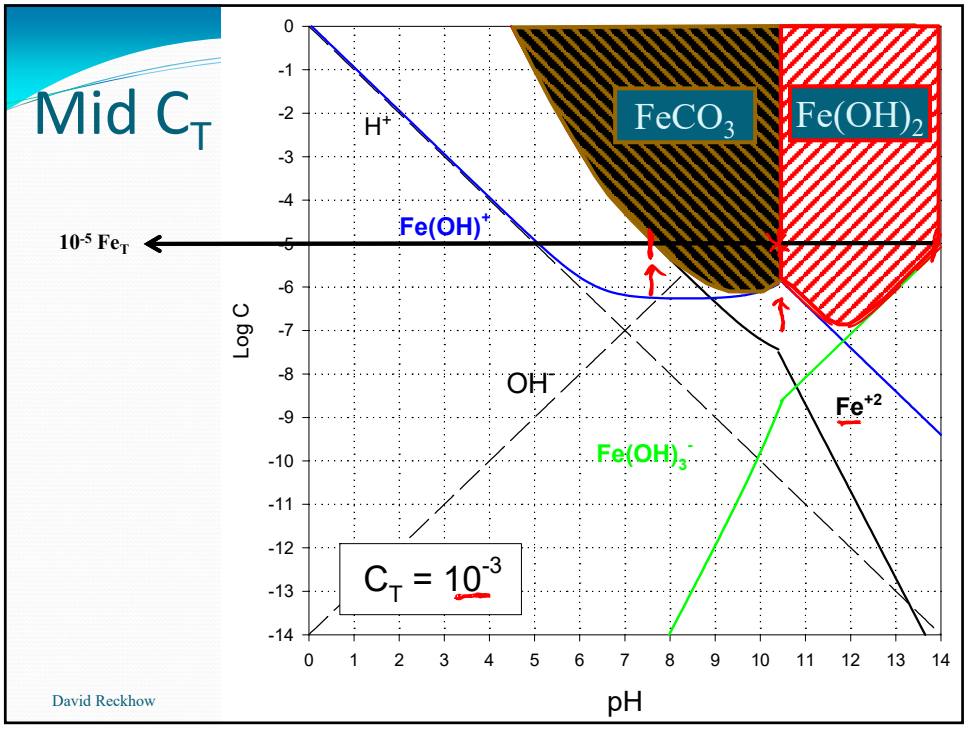
Mid C_T
10^{-5} Fe_T
$FeCO_3$
$Fe(OH)_2$
H^+
$Fe(OH)^+$
OH^-
Fe^{+2}
$Fe(OH)_3^-$
$C_T = 10^{-3}$
Log C
pH
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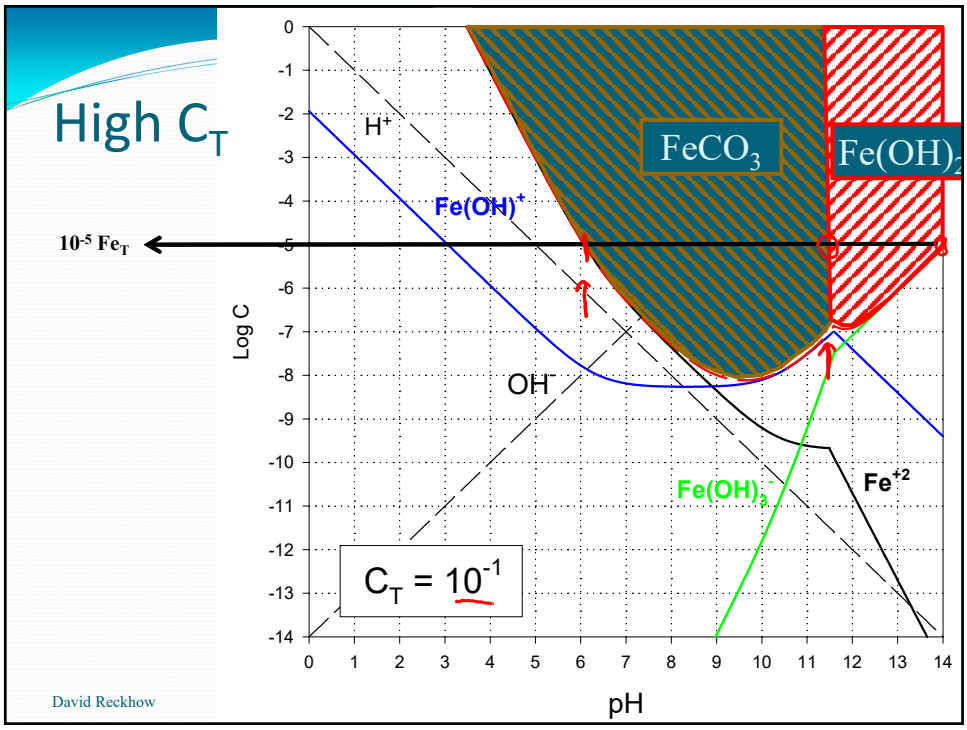
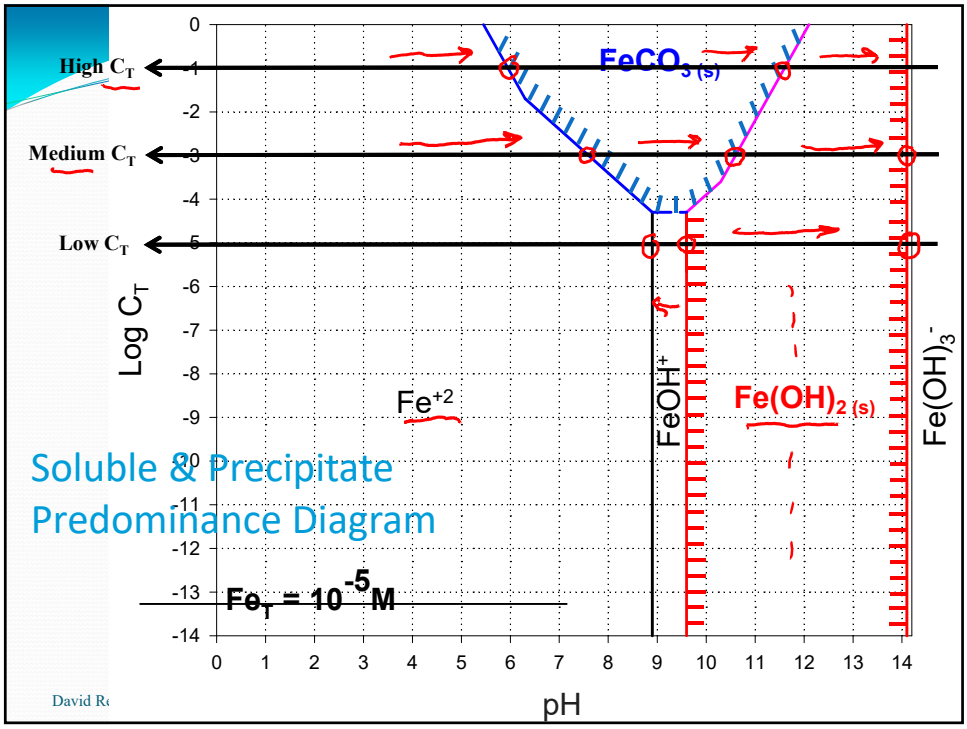

High C_T
10^{-5} Fe_T
$FeCO_3$
$Fe(OH)_2$
H^+
$Fe(OH)^+$
OH^-
Fe^{+2}
$Fe(OH)_3^-$
$C_T = 10^{-1}$
Log C
pH
David Reckhow


High C_T
Medium C_T
Low C_T
Log C_T
$FeCO_{3\,(s)}$
Fe^{+2}
$FeOH^+$
$Fe(OH)_{2\,(s)}$
$Fe(OH)_3^-$
$Fe_T = 10^{-5}$ M
pH
Soluble & Precipitate
Predominance Diagram
David R

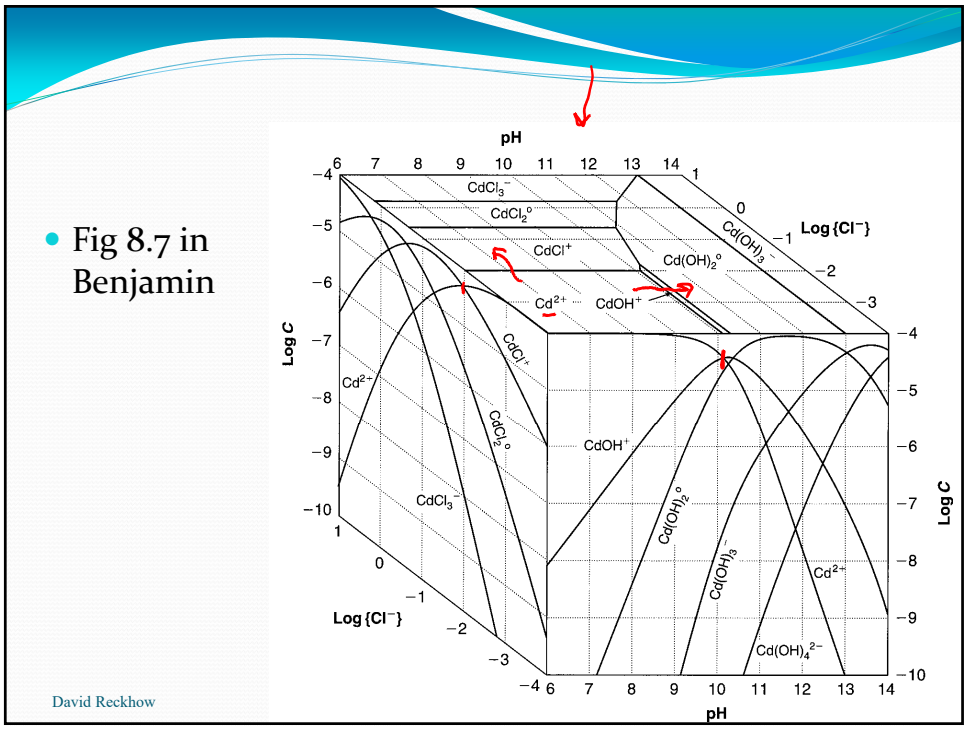


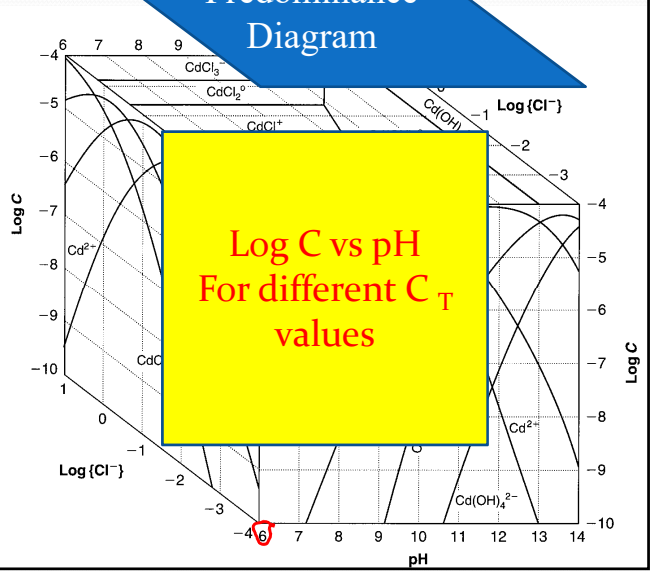
Fig 8.7 in Benjamin
pH
Log C
Log {Cl⁻}
$CdCl_3^-$
$CdCl_2^o$
$CdCl^+$
Cd^{2+}
$CdOH^+$
$Cd(OH)_2^o$
$Cd(OH)_3^-$
$Cd(OH)_4^{2-}$
David Reckhow

3-D form

- Fig[illegible]7 in Be[illegible]

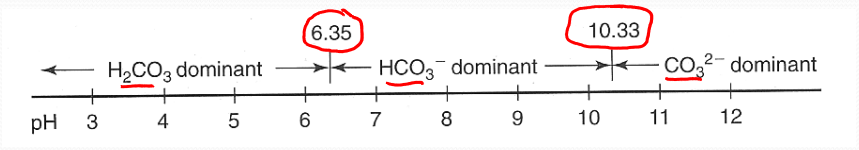
Predominance Diagram

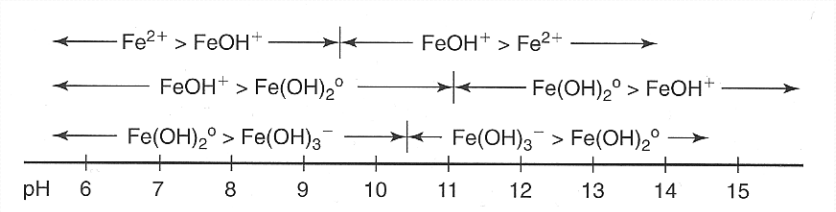
Log C vs Log C_T



Predominance Diagrams: Basics

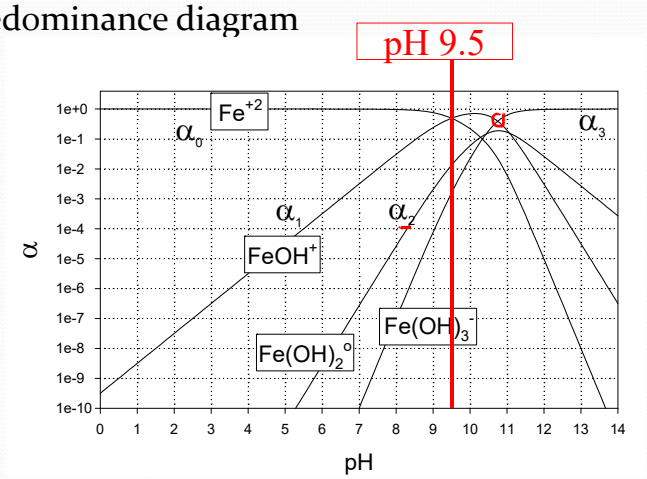
- Soluble species





Ferrous Hydroxides: α diagram

- Soluble predominance diagram



Fe^{+2}, Cl^-, OH^- system I

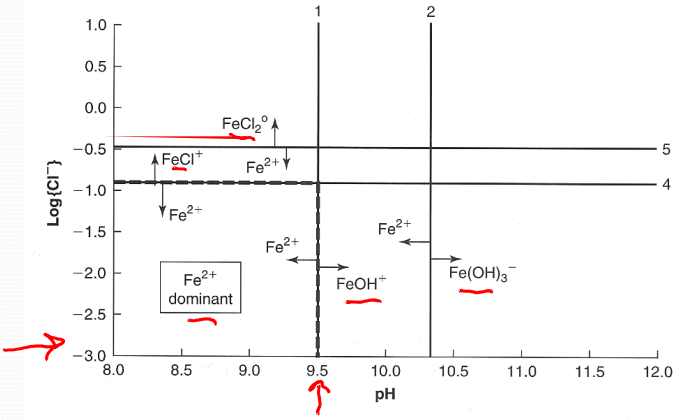


Figure 8.8 Lines showing the four pairwise comparisons between Fe^{2+} and other species in the example system. The arrows indicate the dominant species of the pair on each side of the line. The numbers correspond to the line number column in Table 8.6.

Fe^{+2}, Cl^{-}, OH^{-} system II

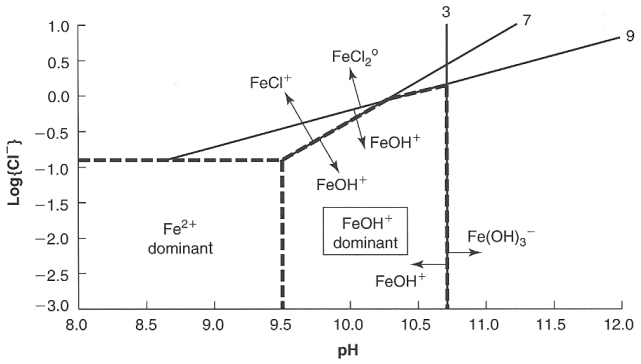
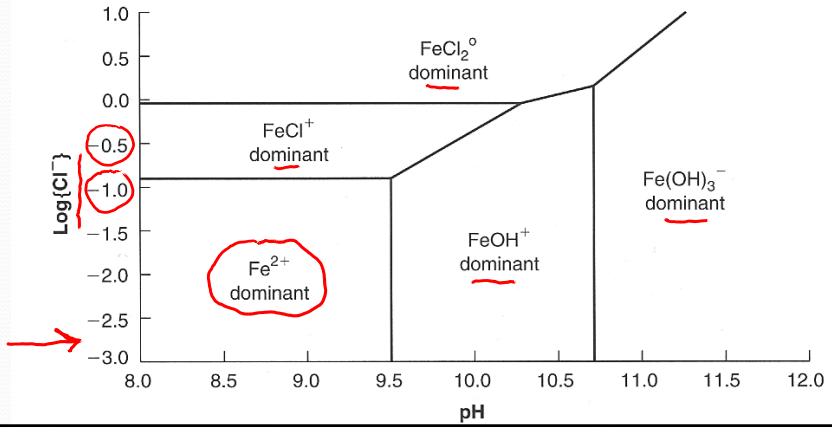


Figure 8.9 Lines showing the pairwise comparisons between $FeOH^+$ and $Fe(OH)_2^o$, $FeCl^+$, or $FeCl_2^o$, and the area of dominance of $FeOH^+$ inferred from those lines.

Fe^{+2}, Cl^{-}, OH^{-} system III

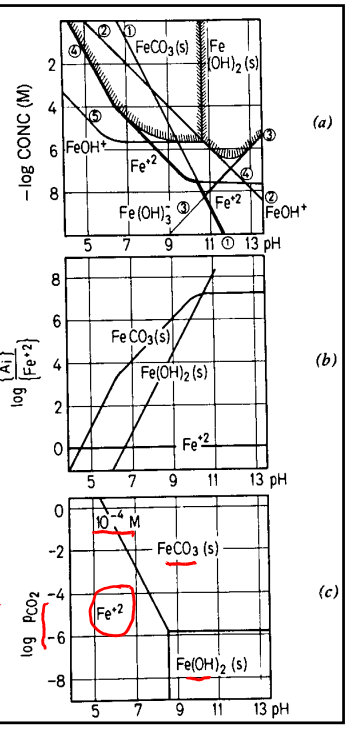
- Final predominance diagram
  - Benjamin Figure 8.10, pg 391



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



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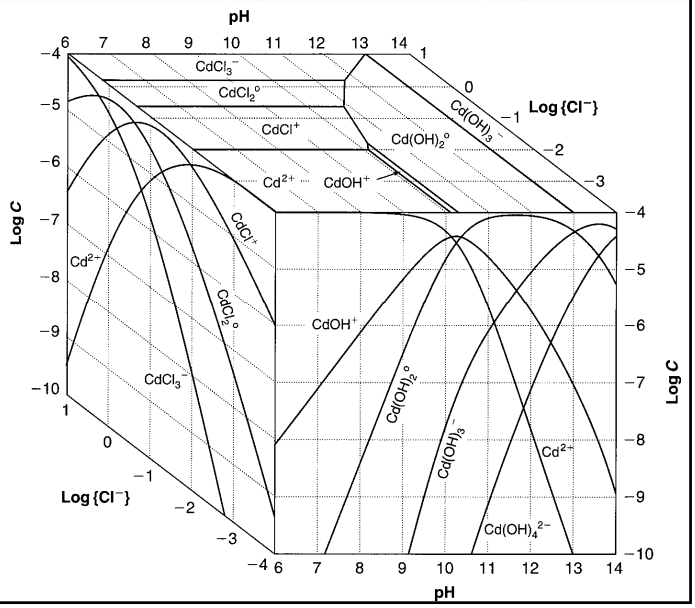
- Fig 8.7 in Benjamin



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Predominance Diagrams with Solid Phases

- Consider Ferrous Carbonate & Ferrous Hydroxide
  - $Fe_T = 10^{-5}$
- Closed System
  - On a Log C_T vs pH axis
- Open system
  - On a Log p_{CO_2} vs pH axis

Predominance Diagrams: Guidance I

- Multiple levels

Benjamin, pg.391

CEE 680 web site

Increasing Complexity

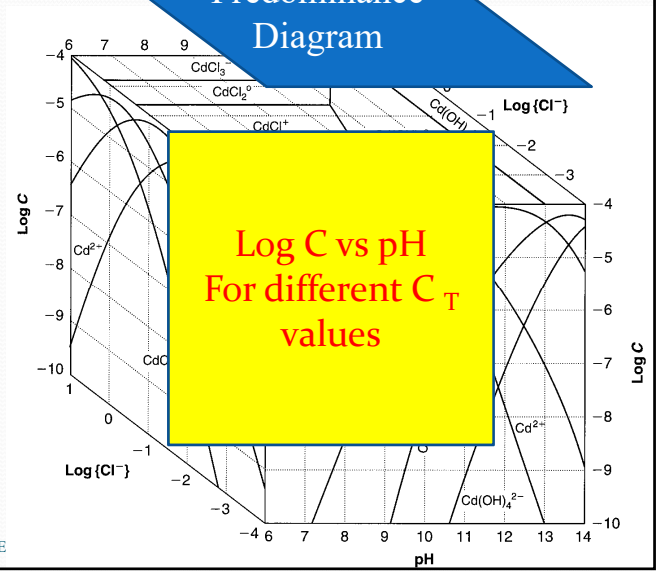
	No solids	1 solid	2 solids	>2 solids
Only OH complexes		$Mg(OH)_2$		Alumino-silicates
Ligand complexes too	$Fe^{+2}/OH^-/Cl^-$	$Fe(OH)_2$, high Cl^-		
pH-dependent ligand speciation			$Fe(OH)_2/FeCO_3$	
Complexing and pH-dependent ligand				

3-D form

- Fig[illegible]7 in Be[illegible]

Predominance Diagram

Log C vs Log C_T



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)

$Fe(OH)_2$ & $FeCO_3$ example I

- Type A lines: concern soluble species
  - Fe^{+2} to $Fe(OH)^+$
    - use first 2 equilibria
    - set species equal to each other

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

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

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

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

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

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

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

$$pH = 8.9$$

Equation #A1

$Fe(OH)_2$ & $FeCO_3$ example II

- Type A lines: concern soluble species
  - $Fe(OH)^+$ to $Fe(OH)_3^-$
    - use 2nd & 3rd equilibria
    - set species equal to each other

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

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

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

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

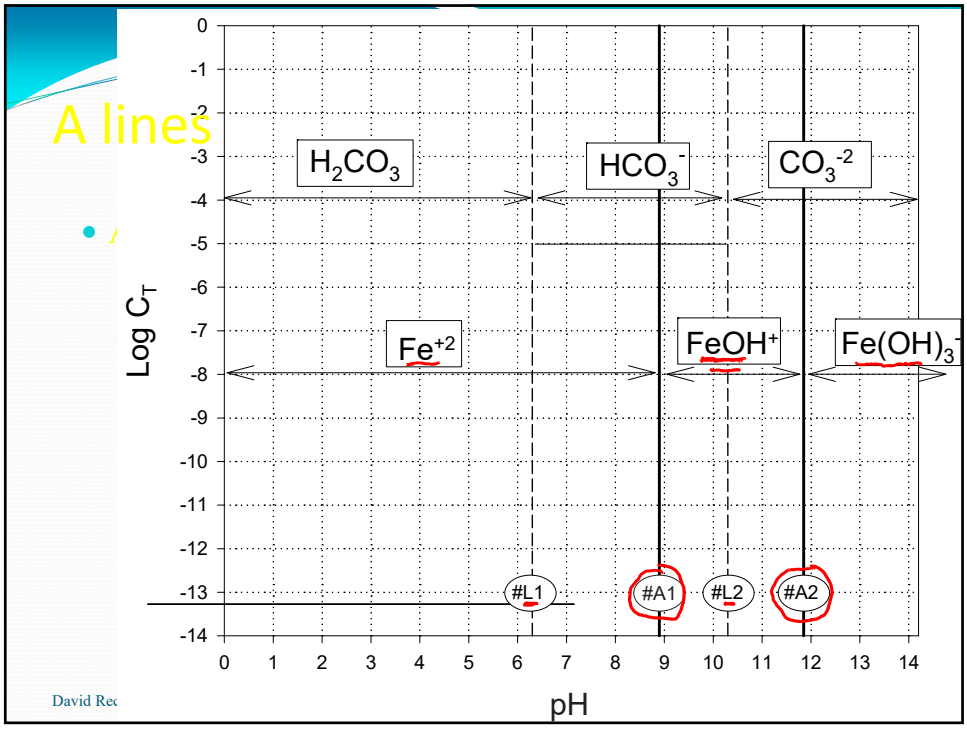
$$10^{-9.4} / [OH^-] = 10^{-5.1}[OH^-]$$

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

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

$$pH = 11.85$$

Equation #A2



$Fe(OH)_2$ & $FeCO_3$ example III

- Type B lines: concern one precipitate
  - $Fe(OH)_{2(s)}$
    - First look at Fe^{+2} and the precipitate

$$10^{-14.5} = [Fe^{+2}][OH^-]^2 = [Fe^{+2}]\left(K_w^2 / [H^+]^2\right)$$

$$[H^+]^2 = 10^{+14.5} K_w^2 [Fe^{+2}] = 10^{-13.5}[Fe^{+2}]$$

$$pH = 6.75 - \tfrac{1}{2}\log[Fe^{+2}]$$

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

$$pH = 6.75 + 2.5 = 9.25$$

But $Fe(OH)^+$ predominates @ pH=8.9-11.85, so this assumption is invalid!

$Fe(OH)_2$ & $FeCO_3$ example IV

- Type B lines: concern one precipitate
  - $Fe(OH)_{2(s)}$
    - Next look at $FeOH^+$ and the precipitate

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

$$[H^+] = 10^{+9.4} K_w [FeOH^+] = 10^{-4.6}[FeOH^+]$$

$$pH = 4.6 - \log[FeOH^+]$$

And assuming, $[FeOH^+] \approx Fe_T = 10^{-5}$, Then:

$$pH = 4.6 + 5.0$$

$$pH = 9.6$$

Again $Fe(OH)^+$ predominates @ pH=8.9-11.85, so now this assumption is valid.

Equation #B1

$Fe(OH)_2$ & $FeCO_3$ example V

- Type B lines: concern one precipitate
  - $Fe(OH)_{2(s)}$
    - Next look at $Fe(OH)_3^-$ and the precipitate

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

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

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

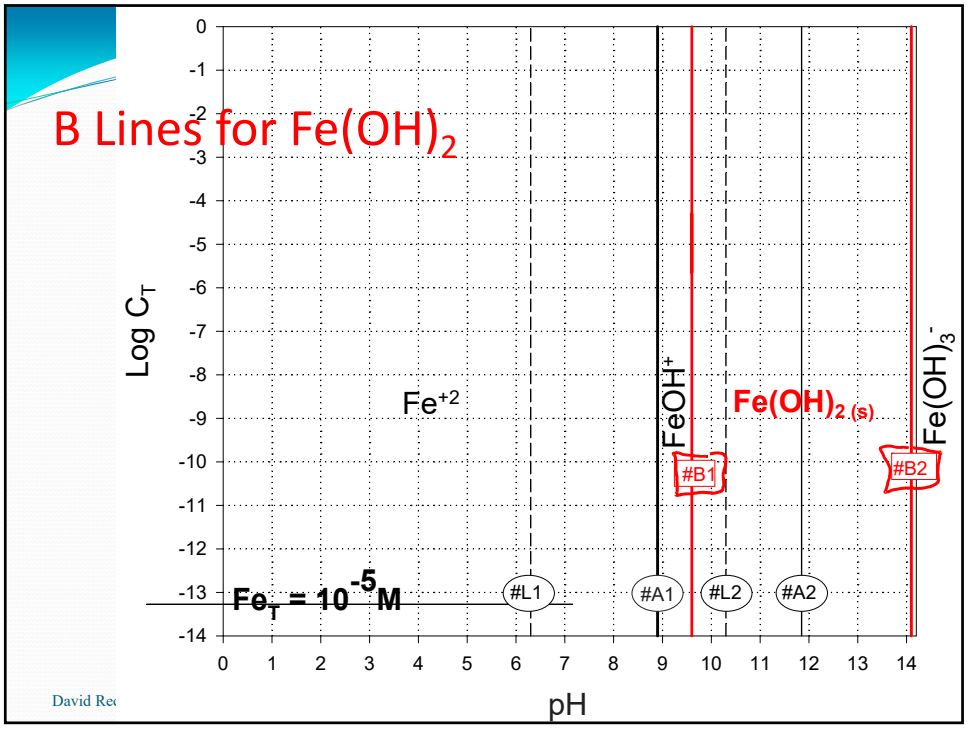
And assuming, $[Fe(OH)_3^-] \approx Fe_T = 10^{-5}$, Then:

$$pH = 19.1 - 5.0$$

$$pH = 14.1$$

$Fe(OH)_3^-$ predominates @ pH>11.85, so this assumption is valid.

Equation #B2



$Fe(OH)_2$ & $FeCO_3$ example VI

- Type B lines for $Fe(CO)_{3(s)}$
  - Incorporates both a metal (Fe) and a ligand (CO_3) 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	Soluble Species Predominance Table
pH for M	<8.9		8.9-11.85	>11.85	
Dominant species	Fe^{+2} H_2CO_3	Fe^{+2} HCO_3^-	$FeOH^+$ HCO_3^-	$FeOH^+$ CO_3^{-2}	$Fe(OH)_3^-$ CO_3^{-2}
pH range	<6.3	6.3-8.9	8.9-10.3	10.3-11.85	>11.85
Equ #	B3a	B3b	B4b	B4c	B5c

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$Fe(OH)_2$ & $FeCO_3$ example VII

- Type B lines
  - $Fe(CO_3)_{(s)}$
    - First look at Fe^{+2} and the precipitate at low pH

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

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

H_2CO_3 predominates @pH<6.3 (Assumption #1)

$$10^{-10.7} = [Fe^{+2}]K_1K_2[H^+]^{-2}C_T$$

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

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

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

Fe^{+2} predominates @ pH<8.9, so the 2 assumptions are only valid in that pH range: <6.3

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

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

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

Equation #B3a → $\log C_T = 10.9 - 2pH$

$Fe(OH)_2$ & $FeCO_3$ example VIII

- Type B lines
  - $Fe(CO_3)_{(s)}$
    - First look at Fe^{+2} and the precipitate at mid pH

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

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

HCO_3^- 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^{+2} predominates @ pH<8.9, so the 2 assumptions are only valid in the pH range; 6.3-8.9

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

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

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

Equation #B3b → $\log C_T = 4.6 - pH$

$Fe(OH)_2$ & $FeCO_3$ example IX

- So far we've looked at the low and mid range pH for Fe^{+2} 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^{+2} and CO_3^{-2} 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^{+2} H_2CO_3	Fe^{+2} HCO_3^-	$FeOH^+$ HCO_3^-	$FeOH^+$ CO_3^{-2}	$Fe(OH)_3^-$ CO_3^{-2}
pH range	<6.3	6.3-8.9	8.9-10.3	10.3-11.85	>11.85
Equ #	B3a	B3b	B4b	B4c	B5c

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

$Fe(OH)_2$ & $FeCO_3$ example X

- Type B lines
  - $Fe(CO_3)_{(s)}$
    - Next look at $FeOH^+$ and the precipitate at mid pH

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

HCO_3^- predominates @pH=6.3-10.3 (Assumption #1)

$$10^{-5.6} = [FeOH^+]K_2[H^+]^{-1}C_T[OH^-]^{-1}$$
$$C_T = 10^{-5.6}[FeOH^+]^{-1}K_2^{-1}[H^+][OH^-]$$
$$= 10^{-5.6}[FeOH^+]^{-1}K_2^{-1}K_w$$
$$\log C_T = -5.6 - pK_w + pK_2 - \log[FeOH^+]$$
$$= -9.3 - \log[FeOH^+]$$

$FeOH^+$ predominates @ pH=8.9-11.85, so the 2 assumptions are only valid in the pH range; 8.9-10.3

Assumption #2, $[FeOH^+] \approx Fe_T = 10^{-5}$, Then:

$$\log C_T = -9.3 - \log Fe_T$$
$$= -9.3 - (-5)$$
$$\log C_T = -4.3$$

Equation #B4b

$Fe(OH)_2$ & $FeCO_3$ example XI

- Type B lines
  - $Fe(CO_3)_{(s)}$
    - Next look at $FeOH^+$ and the precipitate at high pH

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

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

CO_3^{-2} predominates @pH>10.3 (Assumption #1)

$$10^{-5.6} = [FeOH^+]C_T[OH^-]^{-1}$$
$$C_T = 10^{-5.6}[FeOH^+]^{-1}[OH^-]$$
$$= 10^{-5.6}[FeOH^+]^{-1}K_w[H^+]^{-1}$$
$$\log C_T = -5.6 - pK_w - \log[FeOH^+] + pH$$
$$= -19.6 - \log[FeOH^+] + pH$$

Assumption #2, $[FeOH^+] \approx Fe_T = 10^{-5}$, Then:

$$\log C_T = -19.6 - \log Fe_T + pH$$
$$= -19.6 - (-5) + pH$$
$$\log C_T = -14.6 + pH$$

$FeOH^+$ predominates @ pH=8.9-11.85, so the 2 assumptions are only valid in the pH range; 10.3-11.85

Equation #B4c

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$Fe(OH)_2$ & $FeCO_3$ example XII

- At this point we've looked at the 2 relevant pH ranges for Fe^{+2} or $Fe(OH)^+$ and the carbonate precipitate (lines B3a,B3b,B4b and B4c, boxed in table below)
- No need to look at the lowest pH range for $FeOH^+$, and we only need to look at the highest pH range for $Fe(OH)_3^-$ (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^{+2} H_2CO_3	Fe^{+2} HCO_3^-	$FeOH^+$ HCO_3^-	$FeOH^+$ CO_3^{-2}	$Fe(OH)_3^-$ CO_3^{-2}
pH range	<6.3	6.3-8.9	8.9-10.3	10.3-11.85	>11.85
Equ #	B3a	B3b	B4b	B4c	B5c

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

$Fe(OH)_2$ & $FeCO_3$ example XIII

- Type B lines
  - $Fe(CO_3)_{(s)}$
    - Finally look at $Fe(OH)_3^-$ and the precipitate at high pH

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

CO_3^{-2} predominates @pH>10.3 (Assumption #1)

$$10^{-1.3} = [Fe(OH)_3^-]C_T[OH^-]^{-1}$$
$$C_T = 10^{-1.3}[Fe(OH)_3^-]^{-1}[OH^-]^3$$
$$= 10^{-1.3}[Fe(OH)_3^-]^{-1}K_w^3[H^+]^{-3}$$
$$\log C_T = -1.3 - 3pK_w - \log[Fe(OH)_3^-] + 3pH$$
$$= -43.3 - \log[Fe(OH)_3^-] + 3pH$$

$Fe(OH)_3^-$ predominates @ pH>11.85, so the 2 assumptions are only valid in the pH range; >11.85

Assumption #2, $[Fe(OH)_3^+] \approx Fe_T = 10^{-5}$, Then:

$$\log C_T = -43.4 - LogFe_T + 3pH$$
$$= -43.3 - (-5) + 3pH$$

Equation #B5c

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

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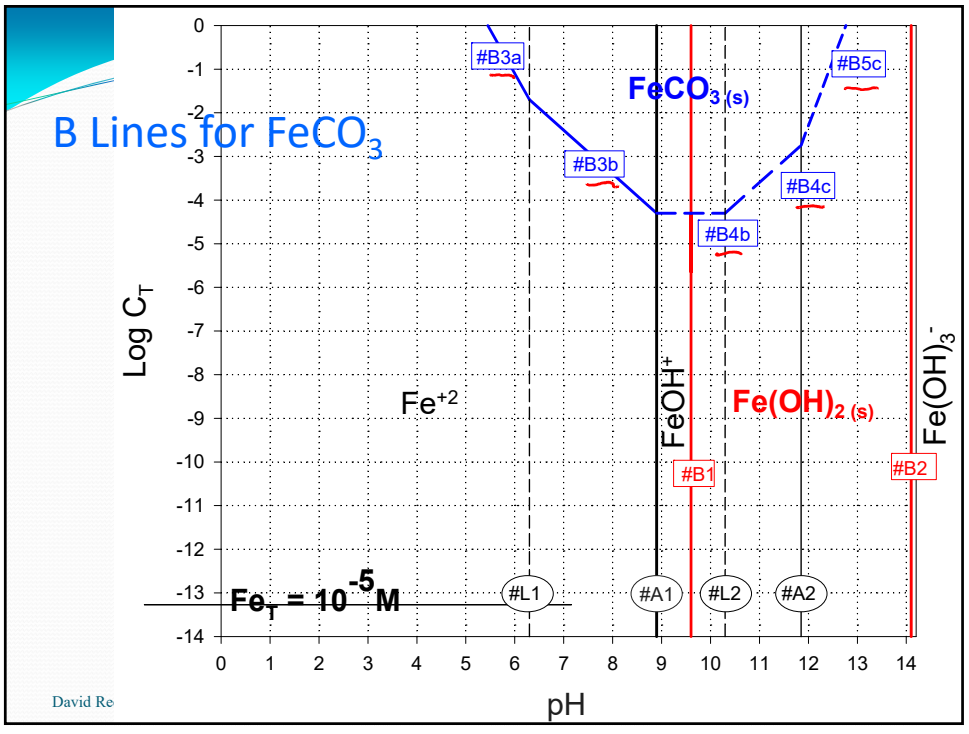


$Fe(OH)_2$ & $FeCO_3$ example XIV

- Type C lines: concern interface between two different precipitates
  - $FeOH_{(s)}$ and $Fe(CO_3)_{(s)}$
    - First look at Fe^{+2} and the precipitate

$Fe(OH)_{2(s)}$ K_{so}

$$10^{-14.5} = [Fe^{+2}][OH^-]^2$$
$$[Fe^{+2}] = 10^{-14.5}[OH^-]^{-2} = 10^{-14.5}K_w^{-2}[H^+]^2$$
$$= 10^{+13.5}[H^+]^2$$

$FeCO_{3(s)}$ K_{so}

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

Use for the C1 lines

$$[CO_3^{-2}] = 10^{-10.7}10^{-13.5}[H^+]^{-2}$$
$$\alpha_2 C_T = 10^{-24.2}[H^+]^{-2}$$
$$\log C_T = -\log \alpha_2 - 24.2 + 2\,pH$$

$Fe(OH)_2$ & $FeCO_3$ example XV

- Type C lines
  - $FeOH_{(s)}$ and $Fe(CO_3)_{(s)}$
    - Both phases exist
      - Assumption #1
    - First look at low pH

H_2CO_3 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.

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

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

H_2CO_3 predominates @pH<6.3 (Assumption #2)

$$\log C_T = -\log(K_1K_2/[H^+]^2) - 24.2 + 2\,pH$$
$$= pK_1 + pK_2 - 24.2$$
$$\log C_T = -7.6$$

Equation #C1a

$Fe(OH)_2$ & $FeCO_3$ example XVI

- Type C lines
  - $FeOH_{(s)}$ and $Fe(CO_3)_{(s)}$
    - Both phases exist
      - Assumption #1
    - Next look at mid pH

HCO_3^- 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.

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

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

HCO_3^- 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

$Fe(OH)_2$ & $FeCO_3$ example XVII

- Type C lines
  - $FeOH_{(s)}$ and $Fe(CO_3)_{(s)}$
    - Both phases exist
      - Assumption #1
    - Lastly look at high pH

CO_3^{-2} 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.

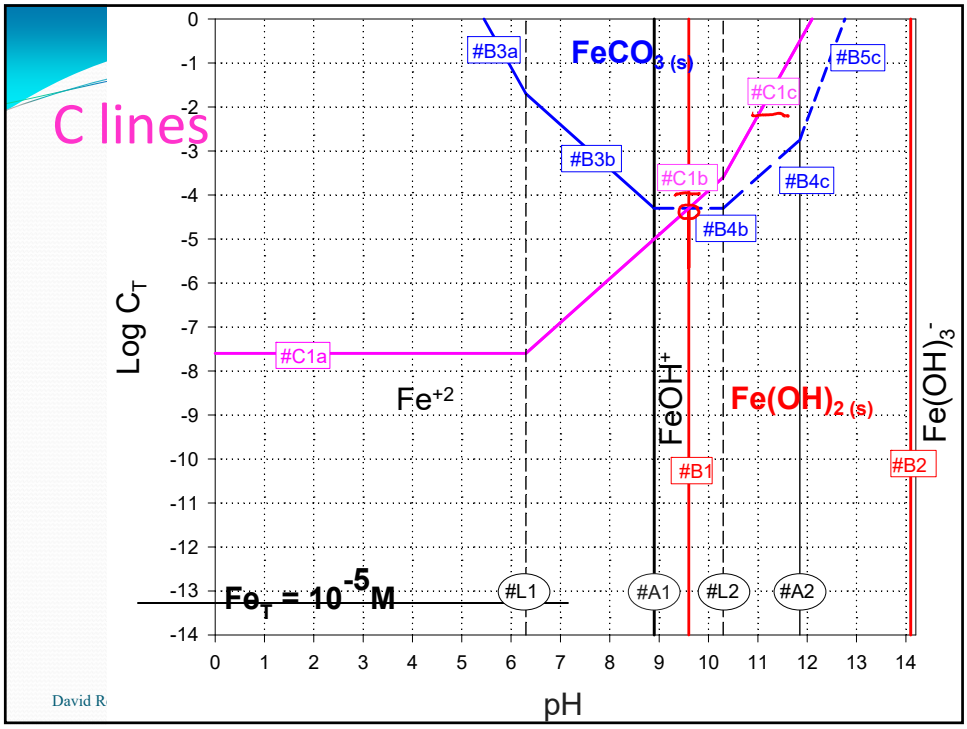
$$\log C_T = -\log \alpha_2 - 24.2 + 2pH$$

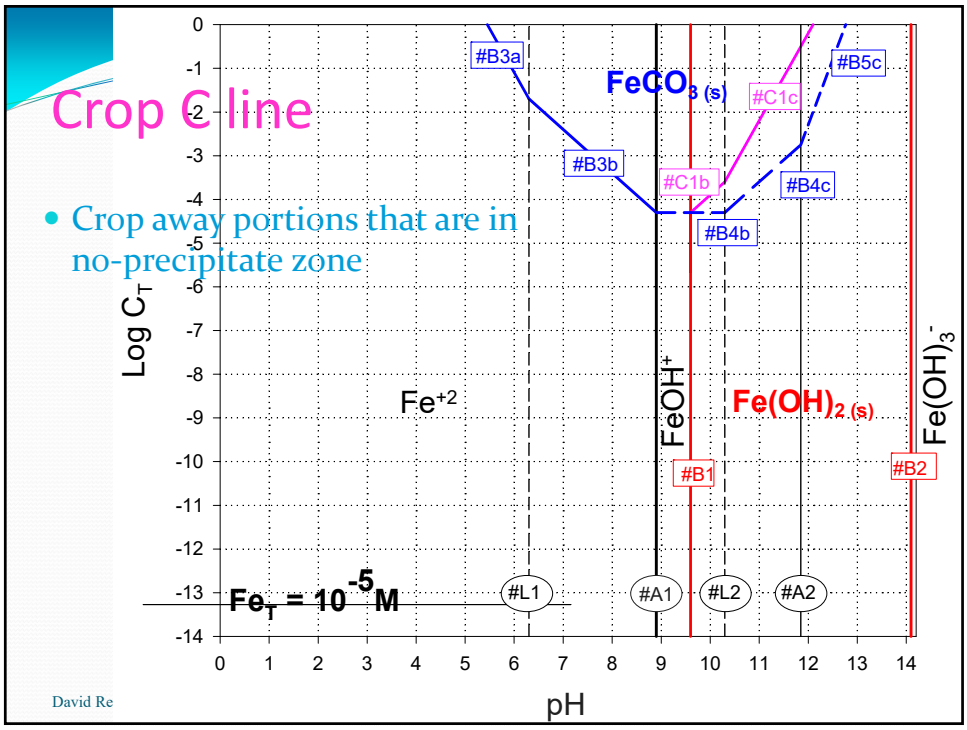
$$\alpha_2 = \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1} \approx 1$$

CO_3^{-2} predominates @pH>10.3 (Assumption #2)

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

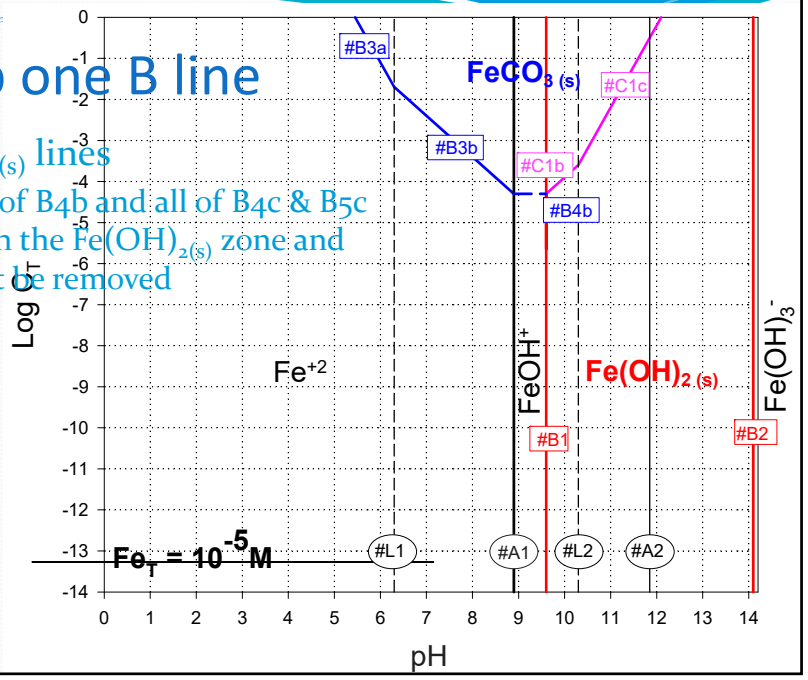
Equation #C1c


C lines
#B3a
FeCO3 (s)
#B5c
#C1c
#B3b
#C1b
#B4c
#B4b
#C1a
Fe+2
FeOH+
Fe(OH)2 (s)
Fe(OH)3-
#B1
#B2
Log CT
FeT = 10-5 M
#L1
#A1
#L2
#A2
pH
David R


Crop C line
• Crop away portions that are in no-precipitate zone
#B3a
FeCO3 (s)
#B5c
#C1c
#B3b
#C1b
#B4c
#B4b
Fe+2
FeOH+
Fe(OH)2 (s)
Fe(OH)3-
#B1
#B2
Log CT
FeT = 10-5 M
#L1
#A1
#L2
#A2
pH
David Re

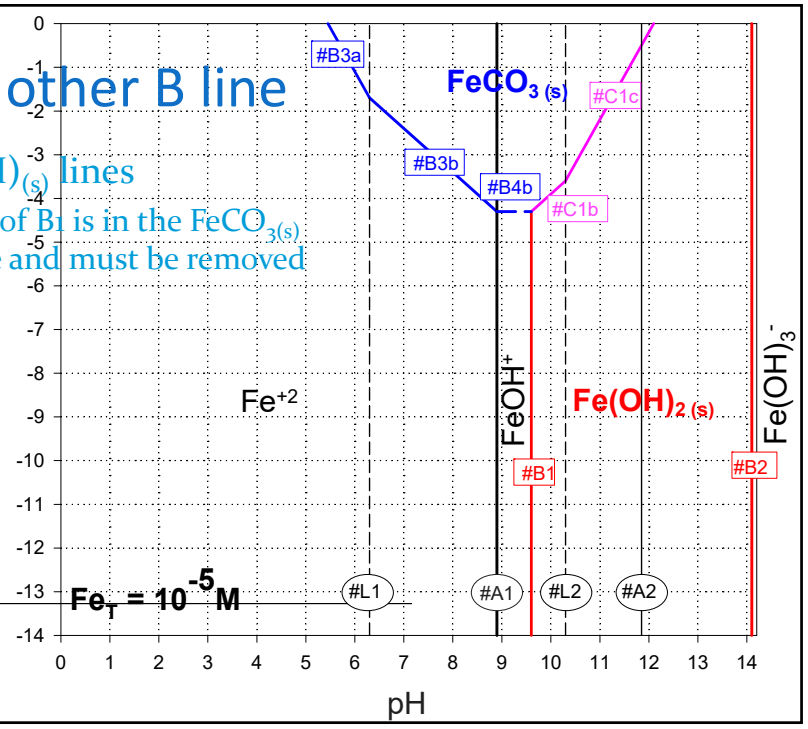
Crop one B line

- $FeCO_{3(s)}$ lines
  - Part of B4b and all of B4c & B5c are in the $Fe(OH)_{2(s)}$ zone and must be removed



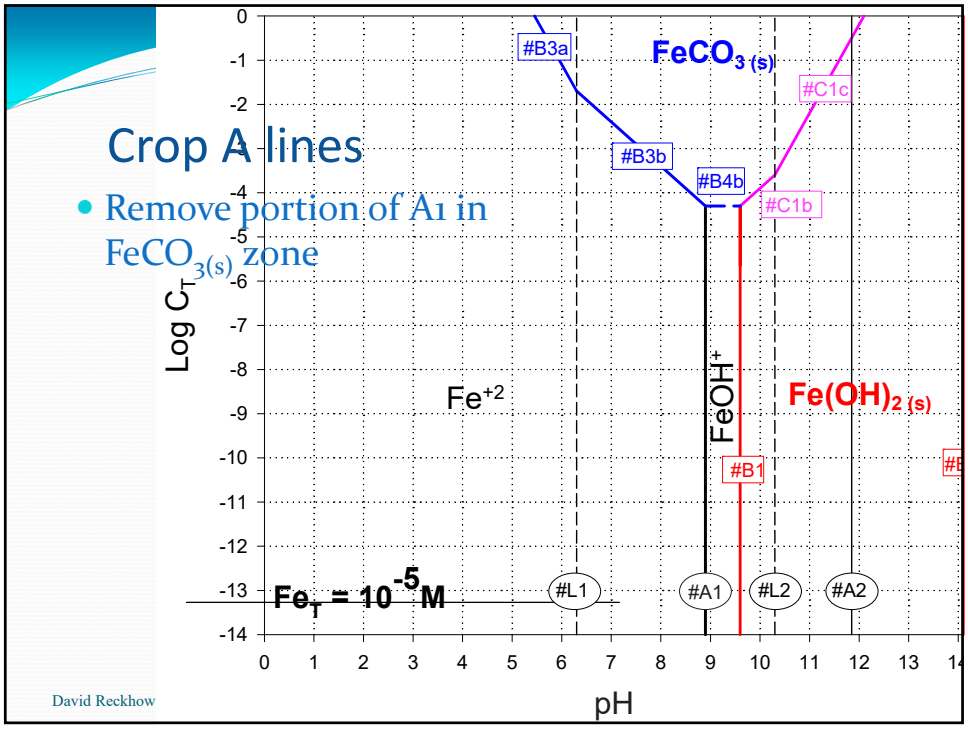
Crop other B line

- $Fe(OH)_{(s)}$ lines
  - Part of B1 is in the $FeCO_{3(s)}$ zone and must be removed

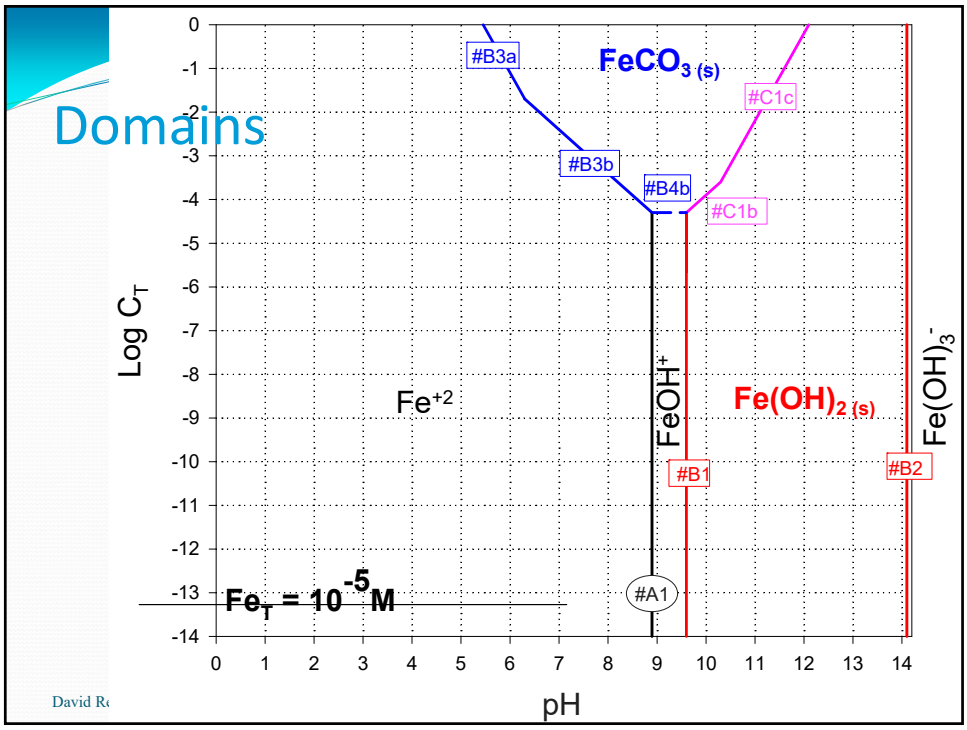


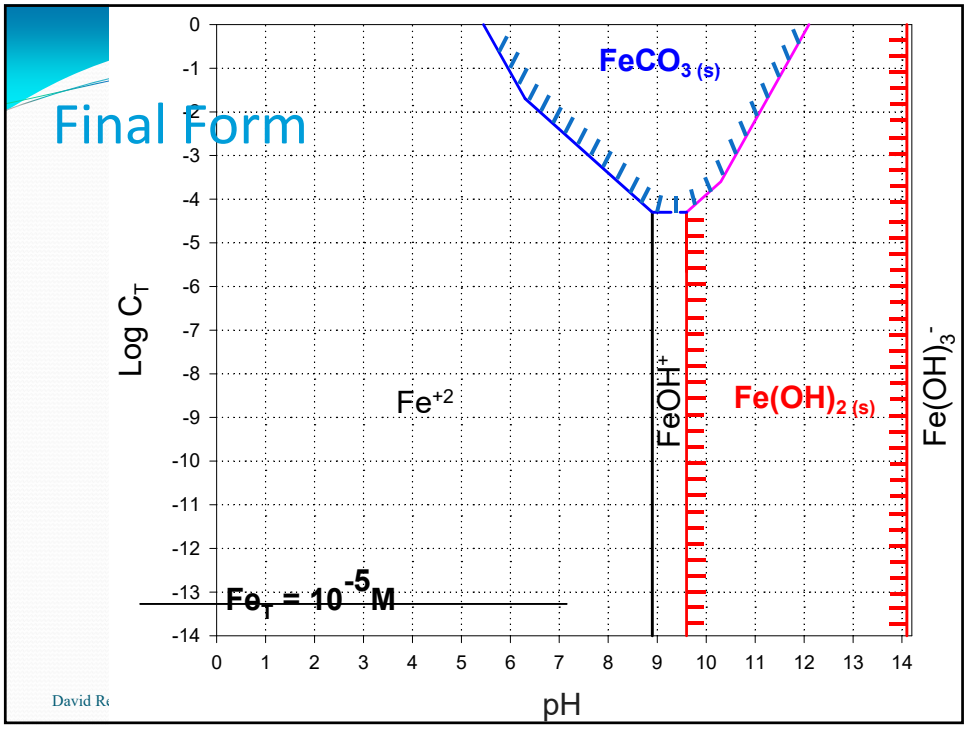
Crop A lines

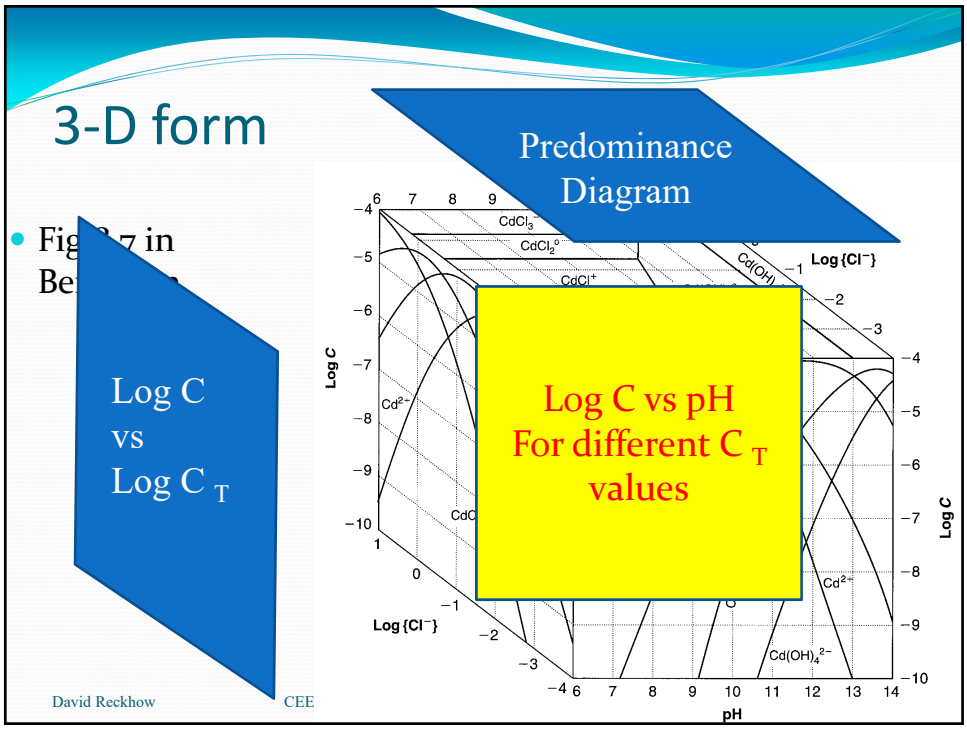
- Remove portion of A1 in $FeCO_{3(s)}$ zone

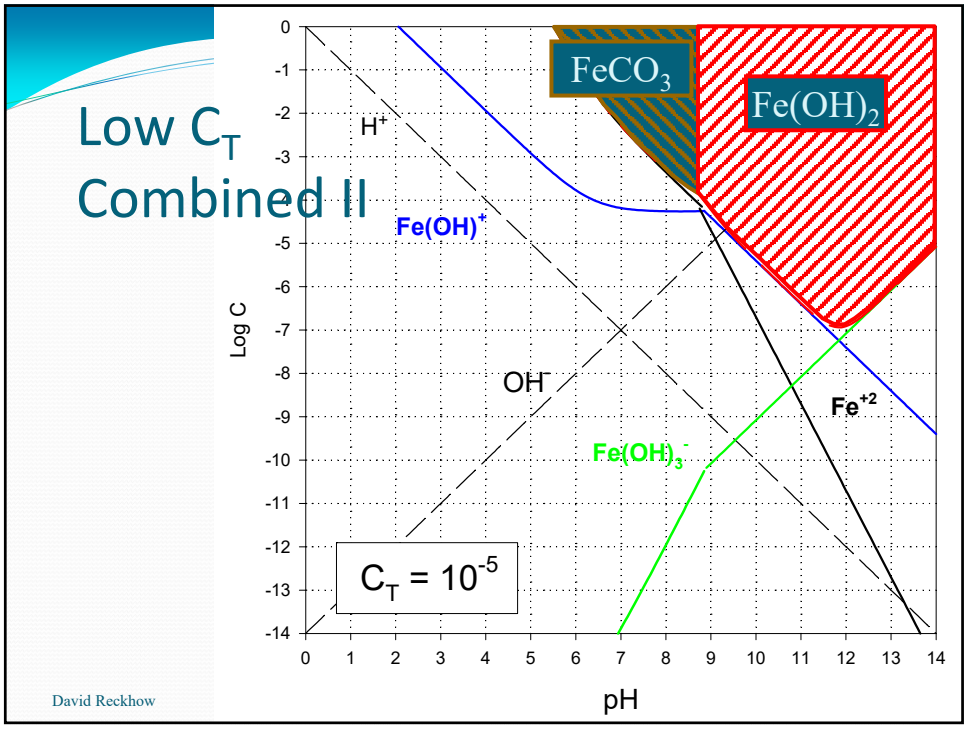


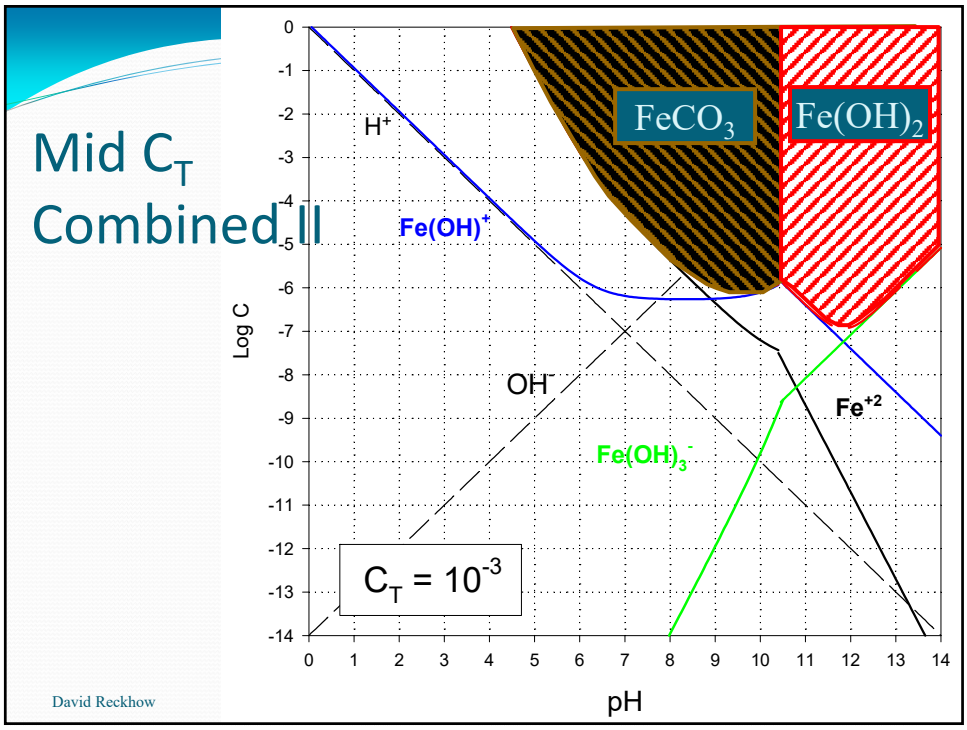
Domains



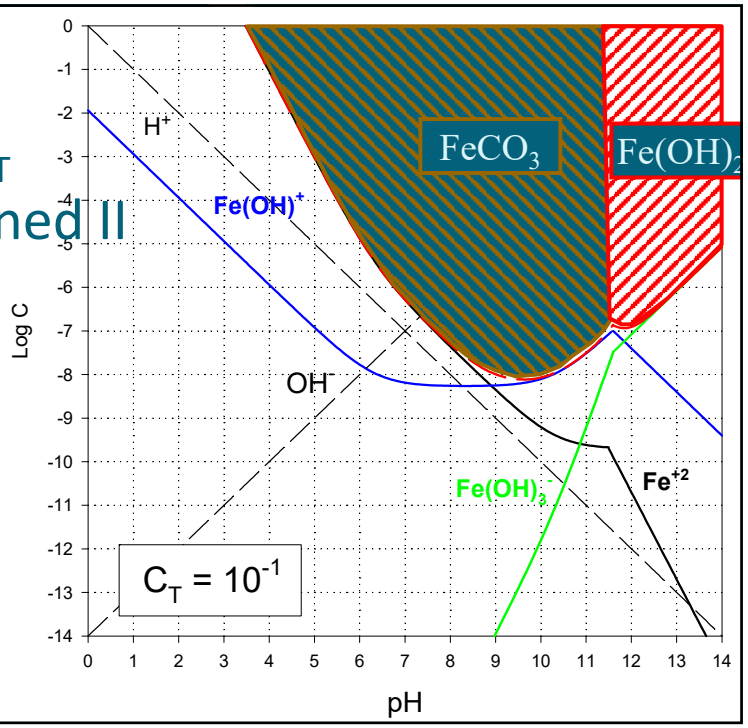

Final Form
FeCO3 (s)
Fe+2
FeOH+
Fe(OH)2 (s)
Fe(OH)3-
Log CT
pH
FeT = 10-5 M
David Re


3-D form
Predominance Diagram
Log C vs Log C T
Log C vs pH For different C T values
Log C
pH
Log {Cl−}
David Reckhow
CEE


Low C_T
Combined II
$FeCO_3$
$Fe(OH)_2$
H^+
$Fe(OH)^+$
OH^-
Fe^{+2}
$Fe(OH)_3^-$
$C_T = 10^{-5}$
Log C
pH
David Reckhow


Mid C_T
Combined II
$FeCO_3$
$Fe(OH)_2$
H^+
$Fe(OH)^+$
OH^-
Fe^{+2}
$Fe(OH)_3^-$
$C_T = 10^{-3}$
Log C
pH
David Reckhow

High C_T Combined II



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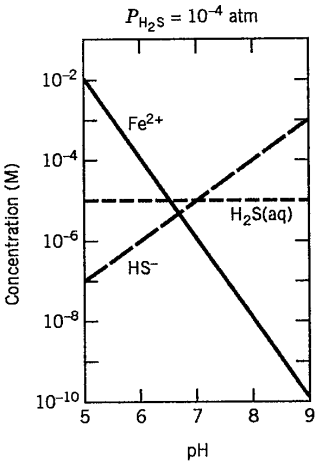
Ferrous Sulfide



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

Table 7.4. Solubility of Sulfides (25°C, $I = 0$)[a]

$$MeS(s) + H^+ = Me^{2+} + HS^- \qquad {}^*K_s = K_{s0}K_2^{-1}$$

$$M_2S(s) + H^+ = 2\,M^+ + HS^- \qquad {}^*K_s = K_{s0}K_2^{-1}$$

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_3S_4	(greigite)[b]	−4.4	Davison (1991)
FeS_2	(pyrite)[c]	−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, sphaelerite)	−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_2S		−34.65	Dyrssen and Kremling (1990)
Ag_2S		−35.94	Dyrssen and Kremling (1990)
Tl_2S		−7.22	Dyrssen and Kremling (1990)

[a]Where necessary, values of K_{s0} were converted into $^*K_s$ by assuming $K_2 = 10^{-13.9}$.
[b]The solubility equilibrium is defined by $Fe_3S_4(s) + 3\,H^+ = 3\,Fe^{2+} + 3\,HS^- + S^0$; $(^*K_s)^3$.
[c]For the equilibrium $FeS_2(s) + H^+ = Fe^{2+} + HS^- + S^0$.

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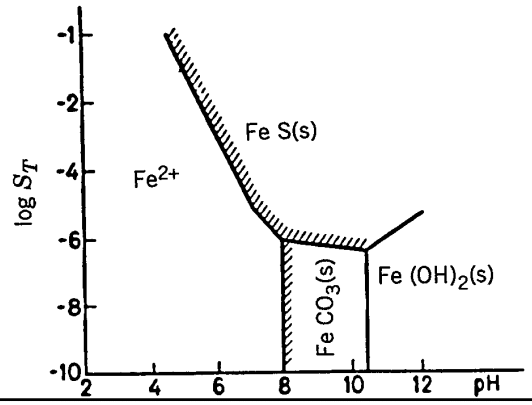
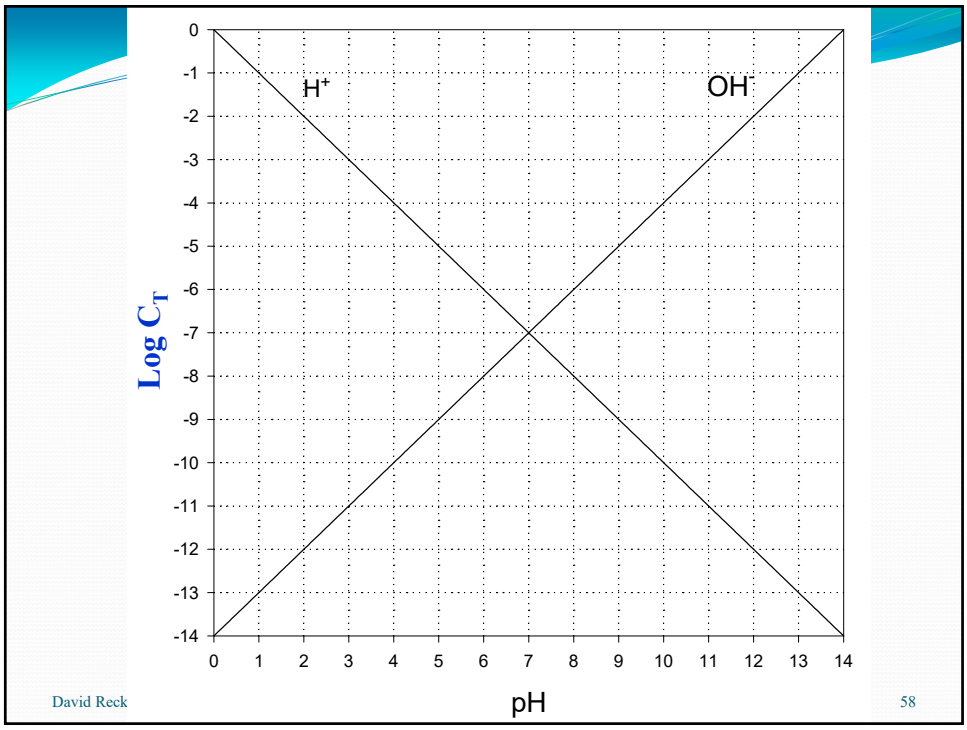
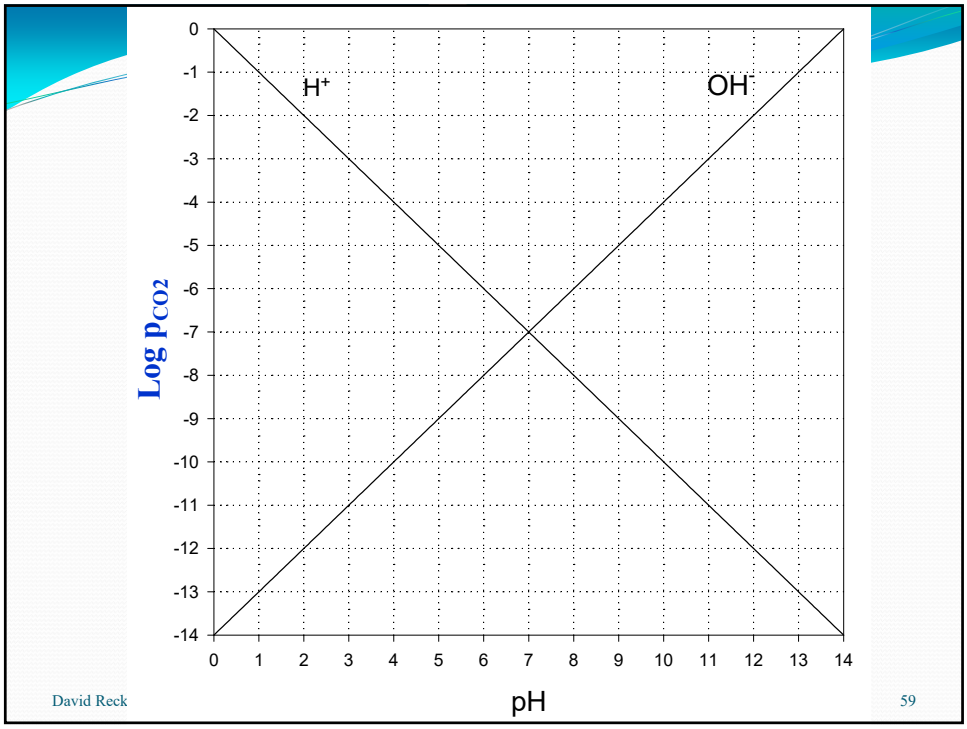


Stumm & Morgan, 1996, Figure 7.18, pg. 403

- To next lecture




H+
OH-
Log pCO2
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
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