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CEE 680: Water Chemistry

Lecture #37

Precipitation and Dissolution: Metal Hydroxides/Oxides & Carbonates

(Stumm & Morgan, Chapt.7)

Benjamin; Chapter 8.7-8.15

Practice Session

- $Al(OH)_3$ ppt
  - Homework
- $Cr(OH)_3$ ppt
- $Zn(OH)_2$ ppt
- $Cd(OH)_2$ ppt

Metal Precipitates; K_{so} values (1/2)

- Table 11.1a in Benjamin (pg 581)

Metal	Mineral Name	Formula	log K_{s0}	Metal	Mineral Name	Formula	log K_{s0}
Ag^+		$AgOH(s)$	−7.70	Cd^{2+}		$Cd(OH)_2(s)$	−14.36
		$Ag_2CO_3(s)$	−11.09		Otavite	$CdCO_3(s)$	−12.01
		$Ag_3PO_4(s)$	−17.59		Greenockite	$CdS(s)$	−31.42
	Acanthite	$Ag_2S(s)$	−53.62			$Cd_3(PO_4)_2(s)$	−32.60
	Cerargyrite	$AgCl(s)$	−9.75	Co^{2+}		$Co(OH)_2(am)$	−14.91
Al^{3+}		$Al(OH)_3(am)$	−31.10			$CoCO_3(s)$	−11.20
	Gibbsite	$Al(OH)_3(s)$	−34.26	Cr^{3+}		$Cr(OH)_3(s)$	−32.65
		$AlPO_4(s)$	−22.50	Cu^{2+}		$Cu(OH)_2(s)$	−18.71
Ca^{2+}	Calcite	$CaCO_3(s)$	−8.48		Tenorite	$CuO(am)$	−19.51
	Aragonite	$CaCO_3(s)$	−8.34		Malachite	$Cu_2(OH)_2CO_3(s)$	−33.47
	Portlandite	$Ca(OH)_2(s)$	−5.30			$CuCO_3(s)$	−11.50
	Lime	$CaO(s)$	−4.70			$Cu_3(PO_4)_2 \cdot 3(H_2O)(s)$	−35.12
	Gypsum	$CaSO_4(s)$	−4.61		Covellite	$CuS(s)$	−39.62
	Hydroxyapatite	$Ca_5(OH)(PO_4)_3(s)$	−58.33	Cu^+		$CuCl(s)$	−6.76

Metal Precipitates; K_{so} values (2/2)

- Table 11.1b in Benjamin (pg 582)

Table 11.1 – *Continued from previous page*

Metal	Mineral Name	Formula	log K_{s0}	Metal	Mineral Name	Formula	log K_{s0}
Fe^{2+}		$Fe(OH)_2(am)$	−14.51	Mn^{2+}		$MnCO_3(am)$	−10.50
	Siderite	$FeCO_3(s)$	−10.59	Ni^{2+}		$Ni(OH)_2(am)$	−17.11
	Vivianite	$Fe_3(PO_4)_2 \cdot 8\,H_2O(s)$	−37.76			$NiCO_3(s)$	−11.20
		$FeS(ppt)$	−20.35			$Ni_3(PO_4)_2(s)$	−31.30
Fe^{3+}	Ferrihydrite	$Fe(OH)_3(s)$	−38.80	Pb^{2+}	Massicot	$PbO(s)$	−15.11
	Goethite	α-$FeOOH(s)$	−41.51		Hydrocerussite	$Pb_3(CO_3)_2(OH)_2(s)$	−46.76
	Lepidocrocite	γ-$FeOOH(s)$	−40.63		Cerussite	$PbCO_3(s)$	−13.20
	Hematite	$Fe_2O_3(s)$	−85.42		Galena	$PbS(s)$	−32.32
	Maghemite	$Fe_2O_3(s)$	−77.61			$Pb_3(PO_4)_2(s)$	−43.53
Hg^{2+}		$Hg(OH)_2(s)$	−24.50	Si^{4+}	Silica	$SiO_2(am, ppt)$	−2.74
	Montroydite	$HgO(s)$	−24.39	Zn^{2+}		$Zn(OH)_2(am)$	−15.53
		$HgCO_3(s)$	−22.52			$ZnCO_3 \cdot H_2O(s)$	−10.26
		$Hg(CN)_2(s)$	−39.28			$Zn_3(PO_4)_2 \cdot 4\,H_2O(s)$	−35.42
	Cinnabar	$HgS(s)$	−56.52		Zincite	$ZnO(s)$	−16.77
Mn^{2+}	Pyrochroite	$Mn(OH)_2(s)$	−12.81		Wurtzite	$ZnS(s)$	−26.02

Metal Hydrolysis

- Table 10.2 in Benjamin
  - Pg 858-859

	i	Log K_i	Log* K_i	Log β_i	Log* β_i
Ag^+	1	2.00	−12.00	2.00	−12.00
	2	2.00	−12.00	4.00	−24.00
Al^{3+}	1	9.01	−4.99	9.01	−4.99
	2	8.89	−5.11	17.90	−10.10
	3	8.10	−5.90	26.00	−16.00
	4	7.00	−7.00	33.00	−23.00
Ca^{2+}	1	1.40	−12.60	1.40	−12.60
Cd^{2+}	1	3.92	−10.08	3.92	−10.08
	2	3.73	−10.27	7.65	−20.35
	3	1.05	−12.95	8.70	−33.30
	4	−0.05	−14.05	8.65	−47.35
Co^{2+}	1	4.80	−9.20	4.80	−9.20
	2	4.90	−9.10	9.70	−18.30
	3	1.10	−12.90	10.80	−31.20
Cr^{3+}	1	10.00	−4.00	10.00	−4.00
	2	8.38	−5.62	18.38	−9.62
	3	6.87	−7.13	25.25	−16.75
	4	2.98	−11.02	28.23	−27.77
Cu^{2+}	1	6.00	−8.00	6.00	−8.00
	2	8.32	−5.68	14.32	−13.68
	3	0.78	−13.22	15.10	−26.90
	4	1.30	−12.70	16.40	−39.60
Fe^{2+}	1	4.50	−9.50	4.50	−9.50
	2	2.93	−11.07	7.43	−20.57
	3	3.57	−10.43	11.00	−31.00
Fe^{3+}	1	11.81	−2.19	11.81	−2.19
	2	10.52	−3.48	22.33	−5.67
	3	6.07	−7.93	28.40	−13.60
	4	6.00	−8.00	34.40	−21.60

	i	Log K_i	Log* K_i	Log β_i	Log* β_i
Hg^{2+}	1	4.50	−9.50	4.50	−9.50
	2	2.93	−11.07	7.43	−20.57
	3	3.57	−10.43	11.00	−31.00
Mg^{2+}	1	2.21	−11.79	2.21	−11.79
Ni^{2+}	1	4.14	−9.86	4.14	−9.86
	2	4.86	−9.14	9.00	−19.00
	3	3.00	−11.00	12.00	−30.00
Pb^{2+}	1	6.29	−7.71	6.29	−7.71
	2	4.59	−9.41	10.88	−17.12
	3	3.06	−10.94	13.94	−28.06
	4	2.36	−11.64	16.30	−39.70
Zn^{2+}	1	5.04	−8.96	5.04	−8.96
	2	6.06	−7.94	11.10	−16.90
	3	2.50	−11.50	13.60	−28.40
	4	1.20	−12.80	14.80	−41.20

$Cd(OH)_2$ example

- Cd species equations
  - From Benjamin, pg 584

$$\log(Cd^{2+}) = 13.64 - 2\,pH \quad (11.14)$$

$$\log(CdOH^{+}) = 3.55 - pH \quad (11.15)$$

$$\log\left(Cd(OH)_2^{\circ}(aq)\right) = -6.65 \quad (11.16)$$

$$\log(Cd(OH)_3^{-}) = -19.66 + pH \quad (11.17)$$

$$\log(Cd(OH)_4^{2-}) = -33.64 + 2\,pH \quad (11.18)$$

$Cd(OH)_2$ solubility diagram

- Pg 586 in Benjamin

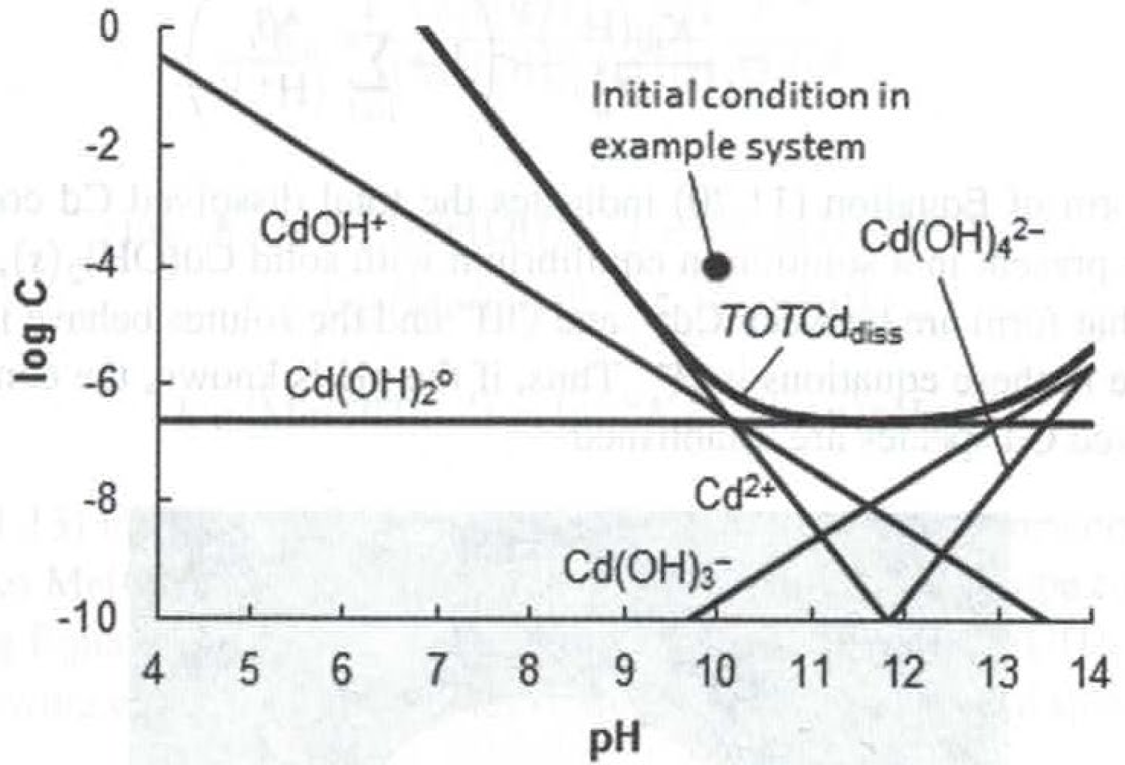


Figure 11.1 Log*C*-pH diagram showing dissolved Cd species in equilibrium with $Cd(OH)_2(s)$. The point identified as the initial condition is for an example presented later in this chapter.

Zinc with OH, CO_3 and Cl

- Pg 636 in Benjamin

Tableau - Visual MINTEQ

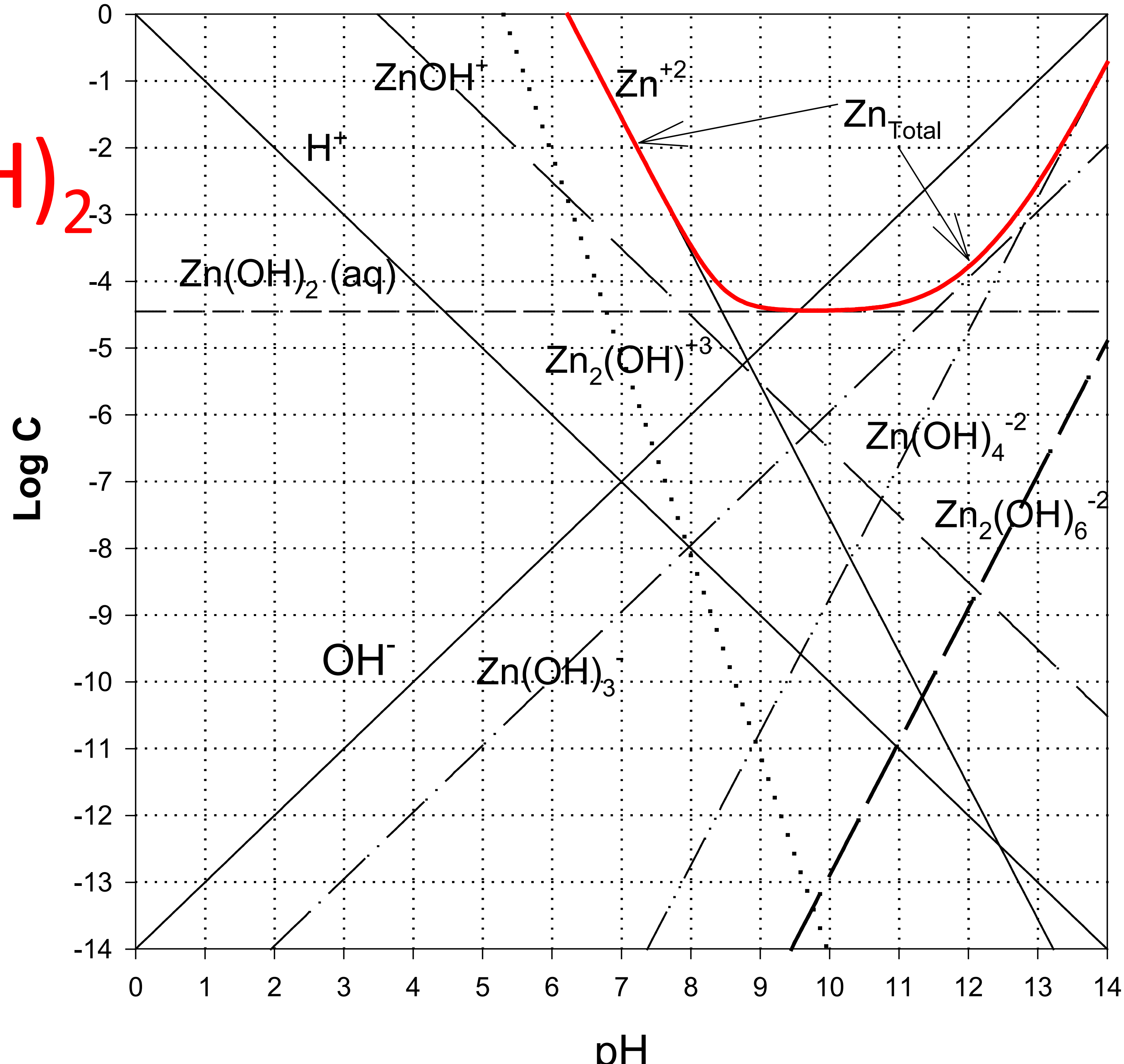
Aqueous species in the present problem

	log K	delta Hr (kJ/mol)	CO3-2	Cl-1	H+1	H2O	Na+1	Zn+2
H2CO3* (aq)	16.681	-32	1	0	2	0	0	0
HCO3-	10.329	-14.6	1	0	1	0	0	0
NaCl (aq)	-.3	-8	0	1	0	0	1	0
NaCO3-	1.27	-20.35	1	0	0	0	1	0
NaHCO3 (aq)	10.029	-28.3301	1	0	1	0	1	0
NaOH (aq)	-13.897	59.81	0	0	-1	1	1	0
OH-	-13.997	55.81	0	0	-1	1	0	0
Zn(CO3)2-2	7.3	0	2	0	0	0	0	1
Zn(OH)2 (aq)	-16.894	0	0	0	-2	2	0	1
Zn(OH)3-	-28.391	0	0	0	-3	3	0	1
Zn(OH)4-2	-41.188	0	0	0	-4	4	0	1
Zn2OH+3	-8.997	63.81	0	0	-1	1	0	2
ZnCl+	.46	5.4	0	1	0	0	0	1
ZnCl2 (aq)	.45	35.6	0	2	0	0	0	1
ZnCl3-	.5	40	0	3	0	0	0	1
ZnCl4-2	.2	45.9	0	4	0	0	0	1
ZnCO3 (aq)	4.76	0	1	0	0	0	0	1

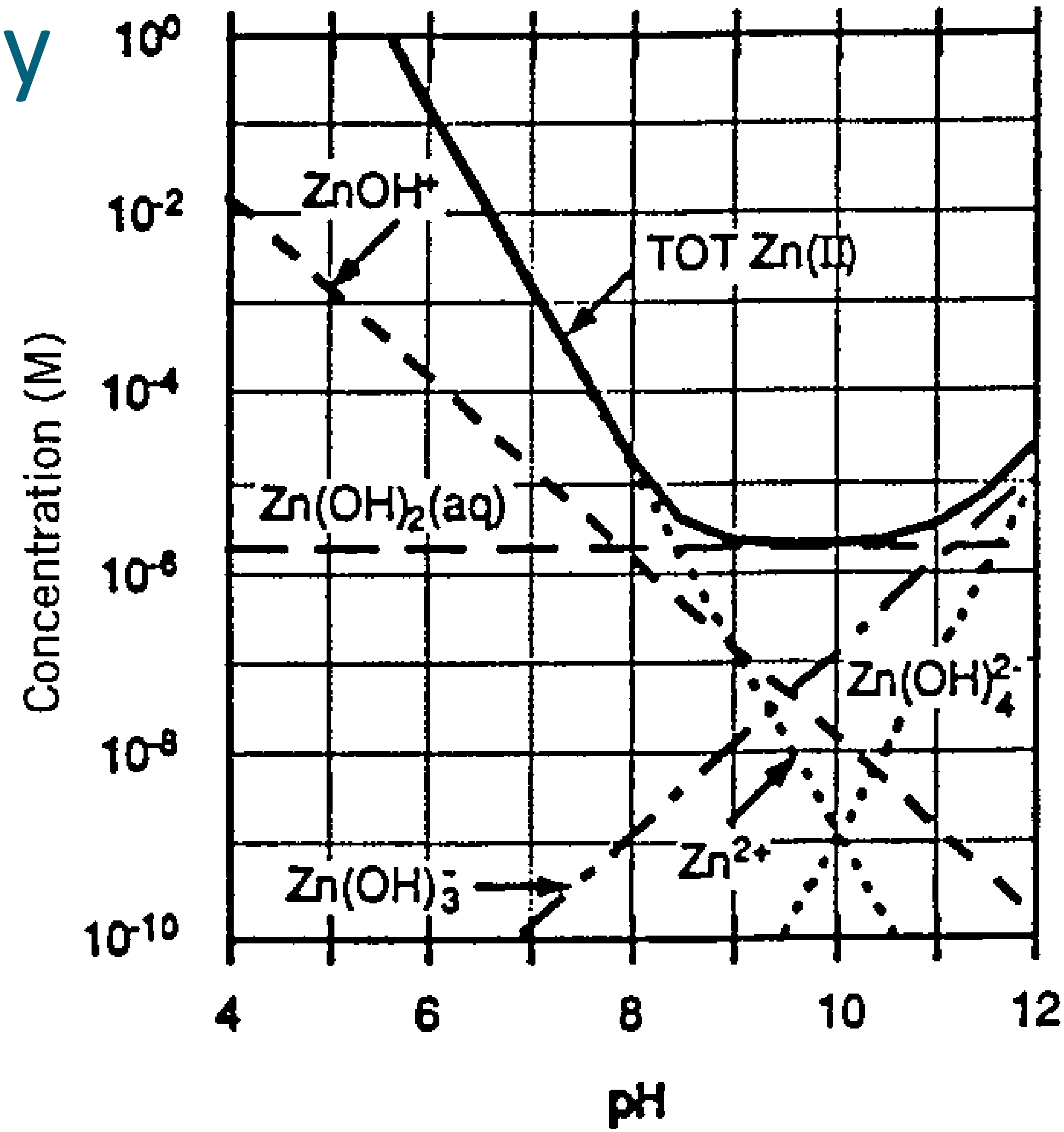
Figure 11.22 Aqueous species considered by Visual Minteq in the simulated titration of $0.02\,M$ Na_2CO_3 with $0.1\,M$ $ZnCl_2$.

$Zn(OH)_2$

- Zn solubility
- Compare to Stumm & Morgan's fig. 6.8c, pg.273



ZnO solubility

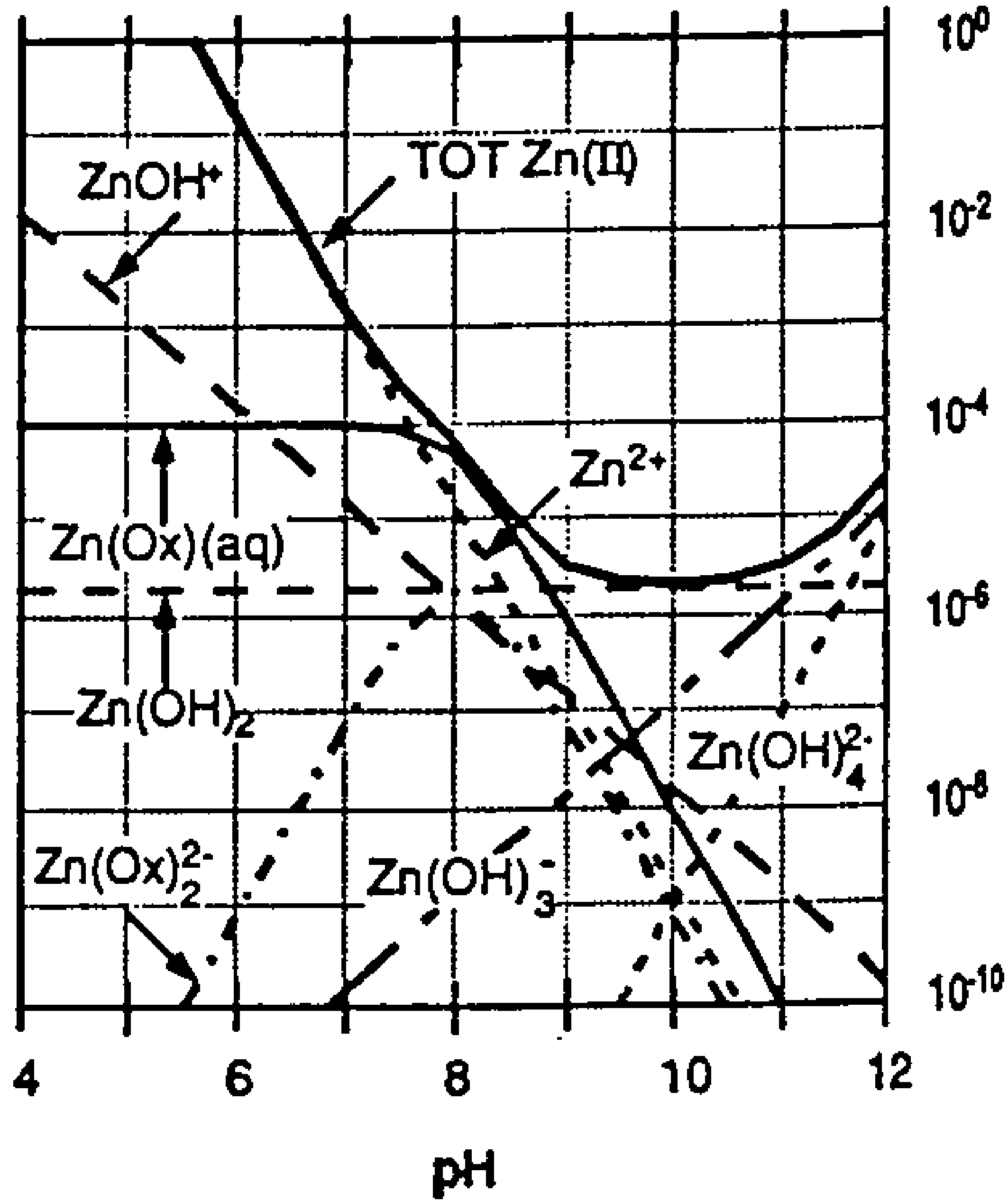


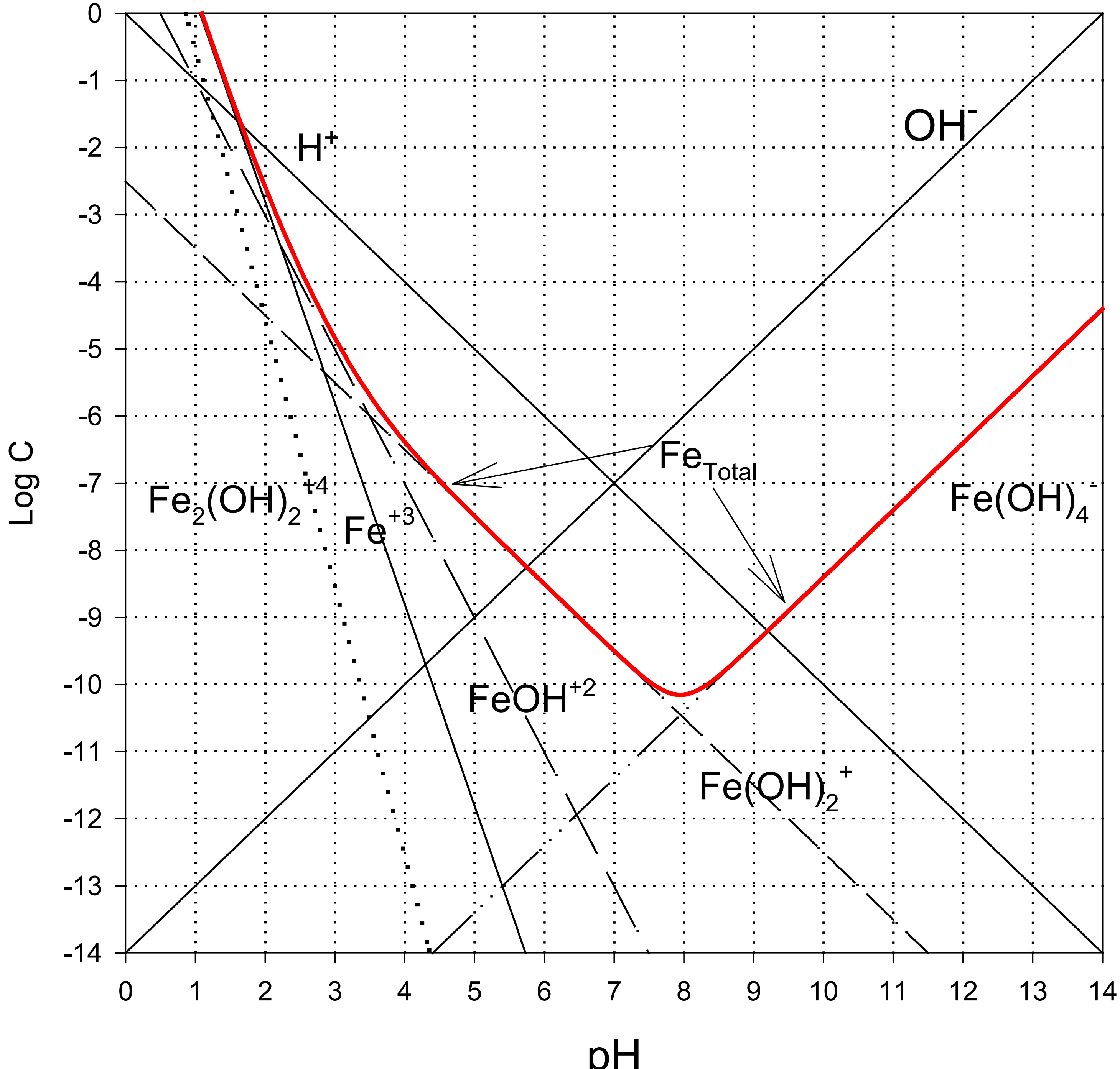
Stumm & Morgan, 1996, Figure 7.6a, pg. 370

ZnO solubility

- With oxalate
  - 10^{-4} M

Stumm & Morgan, 1996, Figure 7.6b, pg. 370

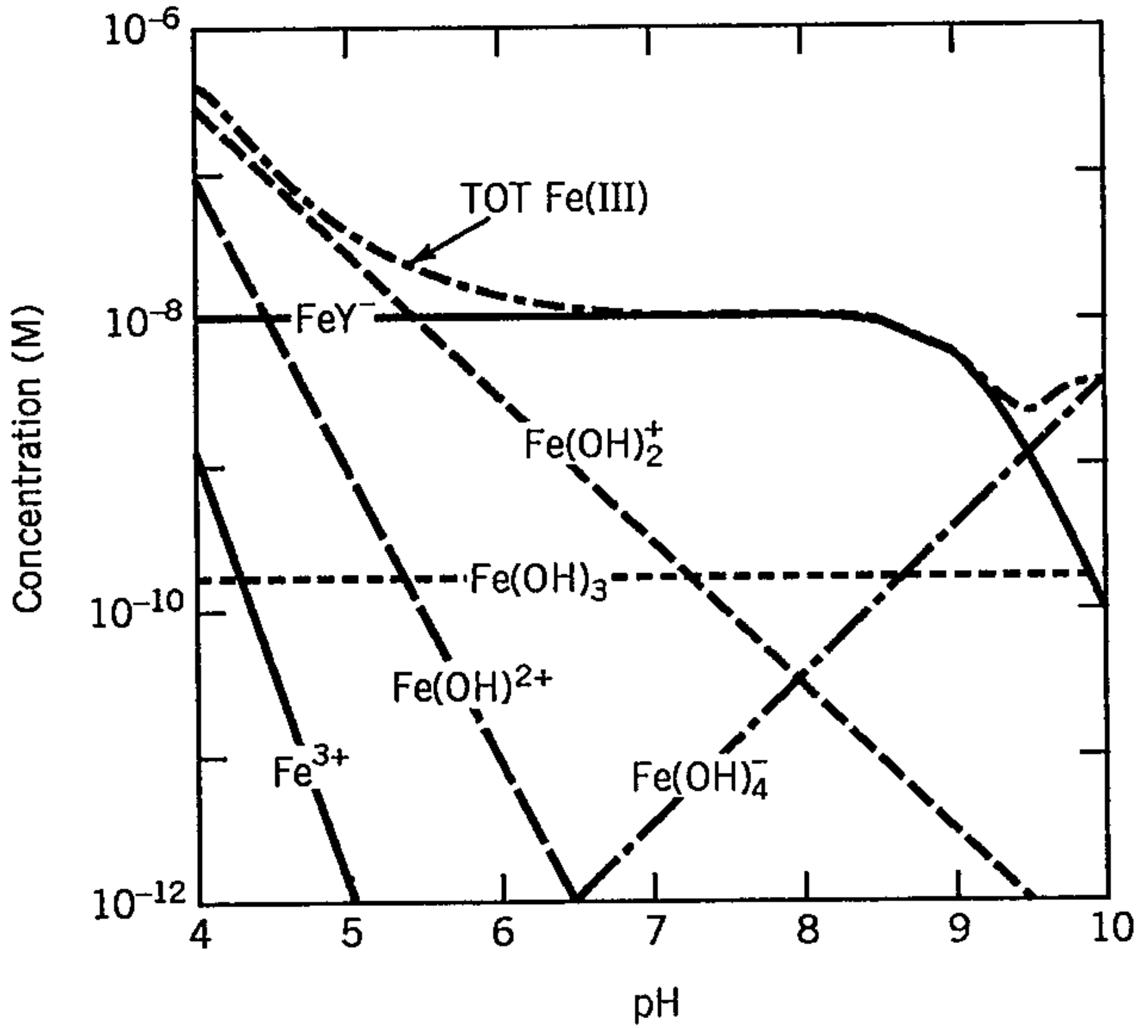




Log C
pH
H+
OH-
Fe2(OH)2+4
Fe+3
FeOH+2
Fe(OH)2+
Fe(OH)4-
FeTotal

Fe with EDTA

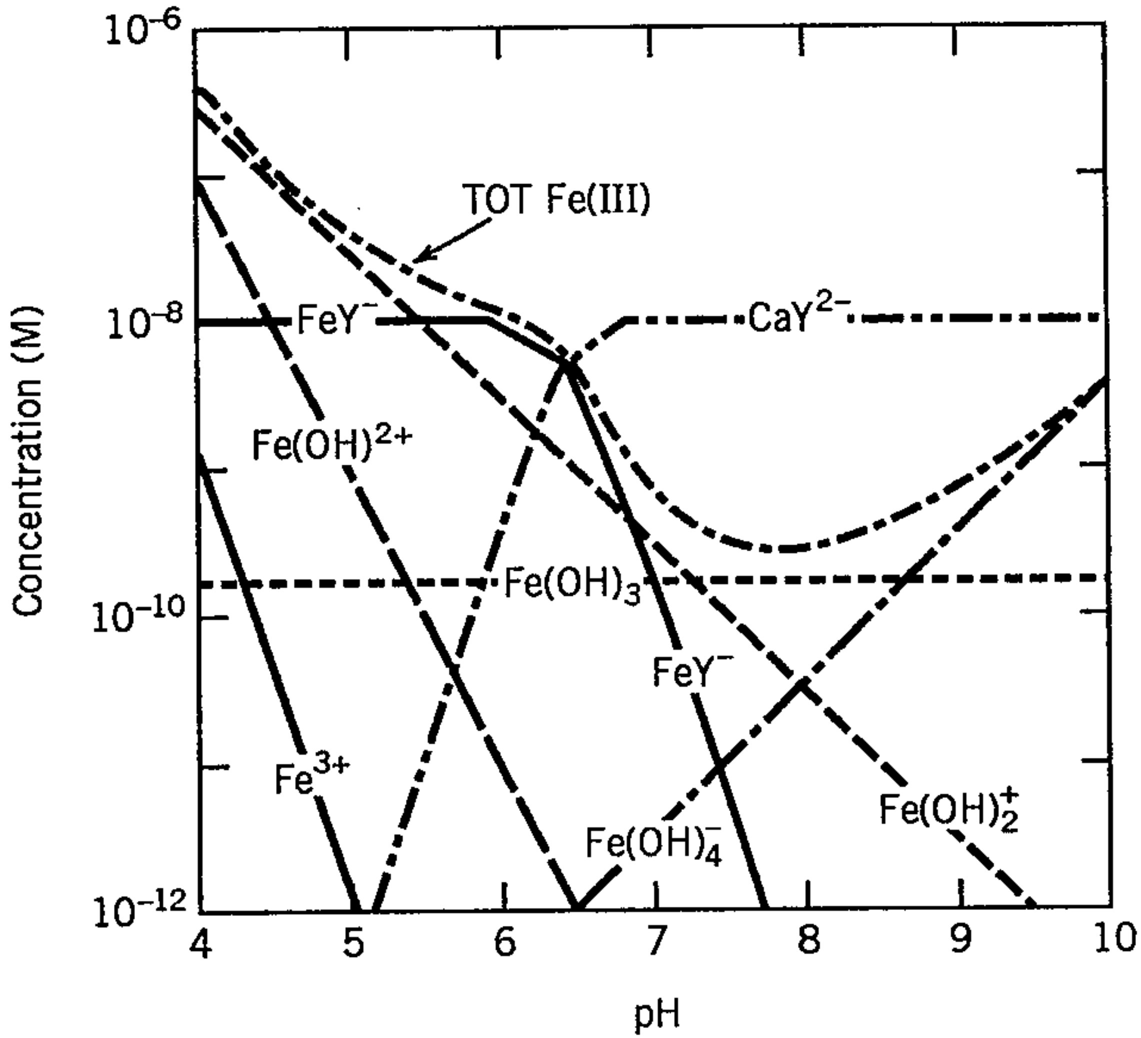
- 10^{-8} M EDTA
  - Elevates solubility in mid-pH range



Stumm & Morgan, 1996, Figure 7.7a, pg. 371

Fe with EDTA & Ca

- 10^{-8} M EDTA
- 10^{-2} M Ca
  - Mostly counteracts affect of EDTA



Stumm & Morgan, 1996, Figure 7.7b, pg. 371

- To next lecture