Updated: 9 March 2020

Print version

CEE 680: Water Chemistry

Lecture #28

Coordination Chemistry: Hydrolysis and Simple Complexes

(Stumm & Morgan, Chapt.6: pg.281-289)

Benjamin; Chapter 8.1-8.6

Stability Constants

- Martell & Smith,1977: *Critical Stability Constants*
  - Vol. 1: Amino Acids
  - Vol. 2: Amines
  - Vol. 3: Other Organic Ligands
  - Vol. 4: Inorganic Complexes
  - Vol. 5: Supplement

HO_2CCO_2H

$C_2H_2O_4$ **Ethanedioic acid (oxalic acid)** H_2L

Metal ion	Equilibrium	Log K 25°, 0.1	Log K 25°, 1.0	Log K 25°, 0	ΔH 25°, 0	ΔS 25°, 0
H^+	HL/H.L	3.82 ±0.04	3.55 ±0.02	4.266 ±0.001	1.60 ±0.06	25.1
		3.55[b] ±0.05		3.80[e]	0.52[c]	18.0[c]
	H_2L/HL.H	1.04 ±0.10	1.04 ±0.04	1.252	0.9 ±0.1	
		1.02[b] ±0.03		1.26[e]		
K^+	ML/M.L			-0.8 [n]		
Be^{2+}	ML/M.L	4.08[h]	3.55			
	$ML_2/M.L^2$	5.38[h]	5.40			
Mg^{2+}	ML/M.L	2.76[h]		3.43[n]		
	$ML_2/M.L^2$	4.24				
Ca^{2+}	ML/M.L		1.66	3.00[n]		
	$ML_2/M.L^2$		2.69			
	MHL/M.HL	1.38		1.84		
	$M(HL)_2/M.(HL)^2$	1.8				
Sr^{2+}	ML/M.L		1.25	2.54[n]		
	$ML_2/M.L^2$		1.90			
	MHL/M.HL	1.11		1.57		
	$M(HL)_2/M.(HL)^2$	1.7				
Ba^{2+}	ML/M.L			2.31[n]		
Sc^{3+}	ML/M.L	8.74[r]	6.86[j]			
	$ML_2/M.L^2$		11.31[j]			
	$ML_3/M.L^3$		14.32[j]			
	$ML_4/M.L^4$		16.70[j]			
	MHL/M.HL	7.36[r]				
Y^{3+}	ML/M.L	5.46				
	$ML_2/M.L^2$	9.29				
La^{3+}	ML/M.L	4.71	4.3			
	$ML_2/M.L^2$	7.83	7.9			
	$ML_3/M.L^3$		10.3			
Ce^{3+}	ML/M.L	4.90	4.49[j]	6.52		
	$ML_2/M.L^2$	8.26	7.91[j]	10.48		
	$ML_3/M.L^3$		10.30[j]	11.30		
	$ML_4/M.L^4$		11.75[j]			
Pm^{3+}	ML/M.L	5.18				
	$ML_2/M.L^2$	8.78				
Eu^{3+}	ML/M.L	5.36	5.04[j]-0.3			
	$ML_2/M.L^2$	9.04	8.70[j]±0.C			
	$ML_3/M.L^3$		11.45[j]-0.2			
	$ML_4/M.L^4$		13.09[j]			
Gd^{3+}	ML/M.L			7.01		

[b] 25°, 0.5; [c] 25°, 1.0; [e] 25°, 3.0; [h] 20°, 0.1; [j] 20°, 1.0; [n] 18°, 0; [r] 25°. 0.05

$C_2H_2O_4$		Ethanedioic acid (oxalic acid)				H_2L
Metal ion	Equilibrium	Log K 25°, 0.1	Log K 25°, 1.0	Log K 25°, 0	ΔH 25°, 0	ΔS 25°, 0
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		3.55[b] ±0.05		3.80[e]	0.52[c]	18.0[c]
	H_2L/HL.H	1.04 ±0.10	1.04 ±0.04	1.252	0.9 ±0.1	
		1.02[b] ±0.03		1.26[e]		
K^+	ML/M.L			-0.8 [n]		
Be^{2+}	ML/M.L	4.08[h]	3.55			
	$ML_2/M.L^2$	5.38[h]	5.40			
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Sr^{2+}	ML/M.L		1.25	2.54[n]		
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Ba^{2+}	ML/M.L			2.31[n]		
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	$ML_2/M.L^2$		11.31[j]			
	$ML_3/M.L^3$		14.32[j]			
	$ML_4/M.L^4$		16.70[j]			

Sources: Stumm & Morgan, 3rd Ed.

- Pg. 326
  - From Morel & Hering, 1993

Table A6.1. (*Continued*)

	OH		CO_3^{2-}		SO_4^{2-}		Cl^-		Br^-		F^-		NH_3	
Al^{3+}	AlL	9.0												
	AlL_2	18.7									AlL	7.0		
	AlL_3	27.0									AlL_2	12.6		
	AlL_4	33.0									AlL_3	16.7		
	Al_3L_4	42.1									AlL_4	19.1		
	$AlL_3 \cdot s$	33.5												
Fe^{3+}	FeL	11.8			FeL	4.0	FeL	1.5	FeL	0.6	FeL	6.0		
	FeL_2	22.3			FeL_2	5.4	FeL_2	2.1			FeL_2	10.6		
	FeL_4	34.4									FeL_3	13.7		
	Fe_2L_2	25.0												
	$FeL_3 \cdot s$	42.7												
	$FeL_3 \cdot s$	38.8												
Mn^{2+}	MnL	3.4	$MnHL$	12.1	MnL	2.3	MnL	0.6			MnL	1.3	MnL	1.0
	MnL_2	5.8	$MnL \cdot s$	10.4									MnL_2	1.5
	MnL_3	7.2												
	MnL_4	7.7												
	$MnL_2 \cdot s$	12.8												
Fe^{2+}	FeL	4.5	$FeL \cdot s$	10.7	FeL	2.2					FeL	1.4		
	FeL_2	7.4												
	FeL_3	11.0												
	$FeL_2 \cdot s$	15.1												
Co^{2+}	CoL	4.3	$CoL \cdot s$	10.0	CoL	2.4	CoL	0.5			CoL	1.0	CoL	2.0
	CoL_2	9.2											CoL_2	3.5
	CoL_3	10.5											CoL_3	4.4
	$CoL_2 \cdot s$	15.7											CoL_4	5.0
Ni^{2+}	NiL	4.1	$NiL \cdot s$	6.9	NiL	2.3	NiL	0.6			NiL	1.1	NiL	2.7
	NiL_2	9.0											NiL_2	4.9
	NiL_3	12.0											NiL_3	6.6
	$NiL_2 \cdot s$	17.2											NiL_4	7.7
													NiL_5	8.3

Sources: Stumm & Morgan, 2nd Ed.

- Pg. 242

TABLE 5.1 (*continued*)

	Symbol for Equilibrium Constants	log K at 25°C	I
α-$Al(OH)_3(s) + 3H^+ = Al^{3+} + 3H_2O$	$*K_{s0}$	8.5	0
$Al(OH)_3$(amorph) $+ 3H^+ = Al^{3+} + 3H_2O$	$*K_{s0}$	10.8	0
$CuO(s) + 2H^+ = Cu^{2+} + H_2O$	$*K_{s0}$	7.65	0
$Cu^{2+} + OH^- = CuOH^+$	K_1	6.0 (18°C)	0
$Cu^{2+} + 2OH^- = Cu(OH)_2$	K_2	12.8	1
$2Cu^{2+} + 2OH^- = Cu_2(OH)_2^{2+}$	K_{22}	17.0 (18°C)	0
$Cu^{2+} + 3OH^- = Cu(OH)_3^-$	K_3	15.2	0
$Cu^{2+} + 4OH^- = Cu(OH)_4^{2-}$	K_4	16.1	0
$Zn^{2+} + H_2O = ZnOH^+ + H^+$	$*K_1$	− 8.96	0
$Zn^{2+} + 2H_2O = Zn(OH)_2 + 2H^+$	$*\beta_2$	−16.9	0
$Zn^{2+} + 3H_2O = Zn(OH)_3^- + 3H^+$	$*\beta_3$	−28.4	0
$Zn^{2+} + 4H_2O = Zn(OH)_4^- + 4H^+$	$*\beta_4$	−41.2	0
$ZnO + 2H^+ = Zn^{2+} + H_2O$	$*K_{s0}$	11.14	0
$Zn(OH)_2$(amorph) $+ 2H^+ = Zn^{2+} + 2H_2O$	$*K_{s0}$	12.45	0
$Cd^{2+} + H_2O = CdOH^+ + H^+$	$*K_1$	−10.1	0
$Cd^{2+} + 2H_2O + Cd(OH)_2(aq) + 2H^+$	$*\beta_2$	−20.4	0
$Cd^{2+} + 3H_2O = Cd(OH)_3^- + 3H^+$	$*\beta_3$	< -33.3	0
$Cd^{2+} + 4H_2O = Cd(OH)_4^{2-} + 4H^+$	$*\beta_4$	−47.4	0

Reconciling the constants: $Al(OH)_3$

- S&M:3rd Edition
  - AlL_3 s $10^{33.5}$

$$\frac{AlL_3(s)}{Al \bullet L^3} = 10^{33.5}$$

$$10^{-33.5} = [Al^{+3}][OH^-]^3 = [Al^{+3}]\frac{K_w^{\ 3}}{[H^+]^3}$$

$$[Al^{+3}] = 10^{-33.5}(10^{-14})^3[H^+]^3$$

$$\log[Al^{+3}] = 8.5 - 3pH$$

- S&M:2nd Edition
  - α-$Al(OH)_3(s) + 3H^+ = Al^{+3} + 3\ H_2O$
    - $^*K_{so}$ 8.5

$$10^{8.5} = \frac{[Al^{+3}]}{[H^+]^3}$$

$$[Al^{+3}] = 10^{8.5}[H^+]^3$$

$$\log[Al^{+3}] = 8.5 - 3pH$$

Metal Hydrolysis

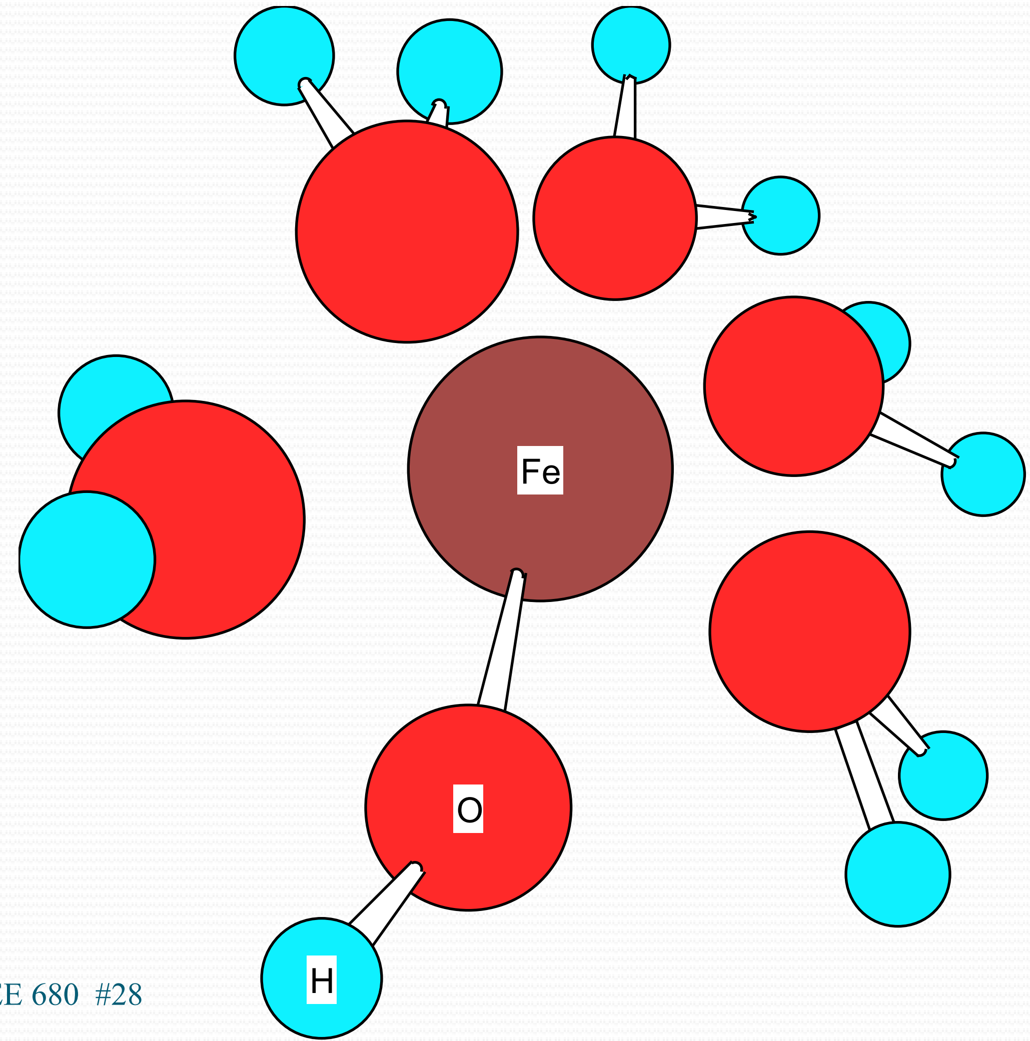
- Case for iron

$$Fe(H_2O)_6^{+3} \leftrightarrow FeOH(H_2O)_5^{+2} + H^+ \leftrightarrow Fe(OH)_2(H_2O)_4^{+} + 2H^+$$

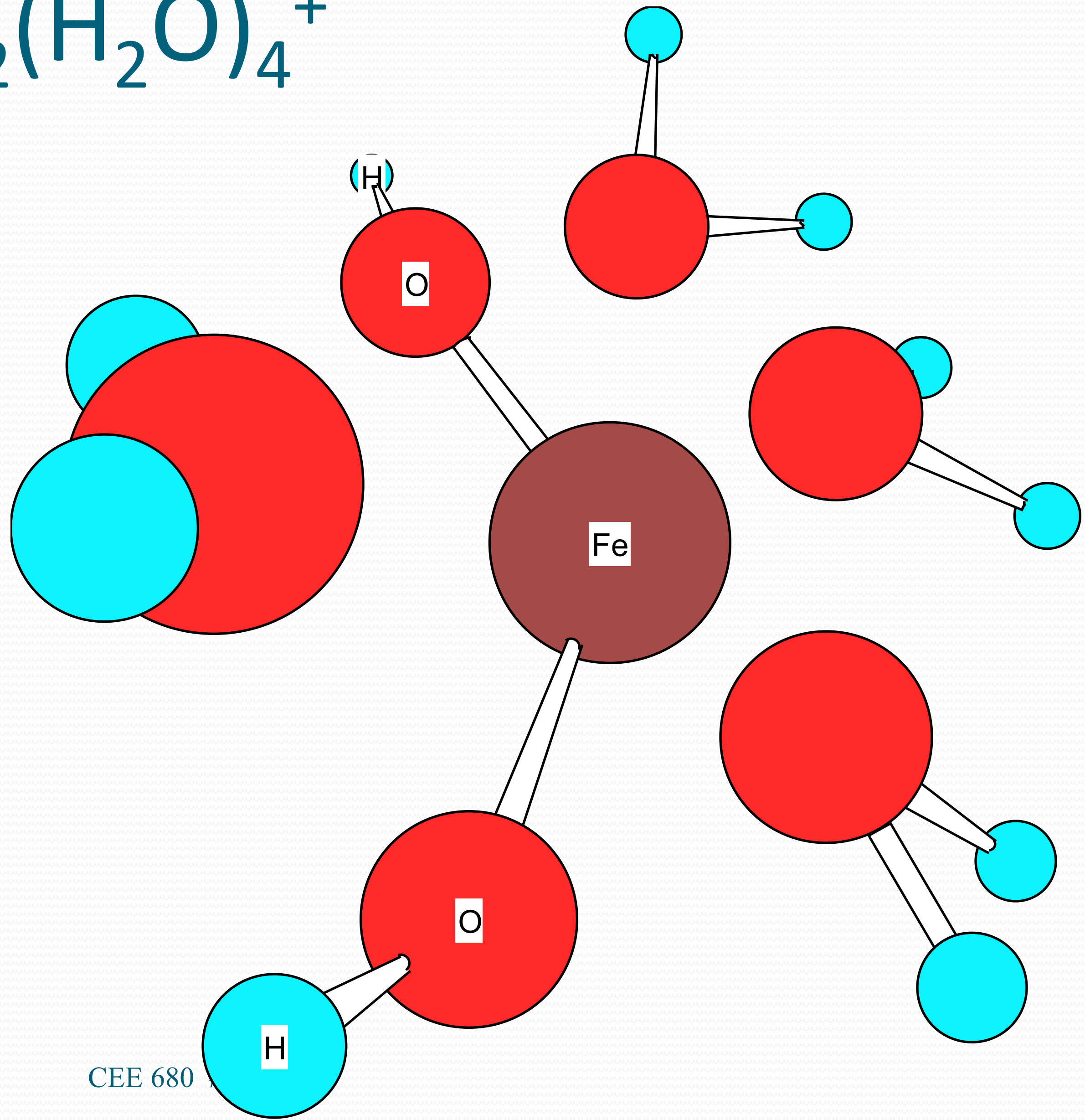
$$\leftrightarrow Fe(OH)_3(H_2O)_3 + 3H^+ \leftrightarrow Fe(OH)_4(H_2O)_2^{-} + 4H^+$$

$$Fe(OH)_3(H_2O)_3 \Downarrow Fe(OH)_3\,(s)$$

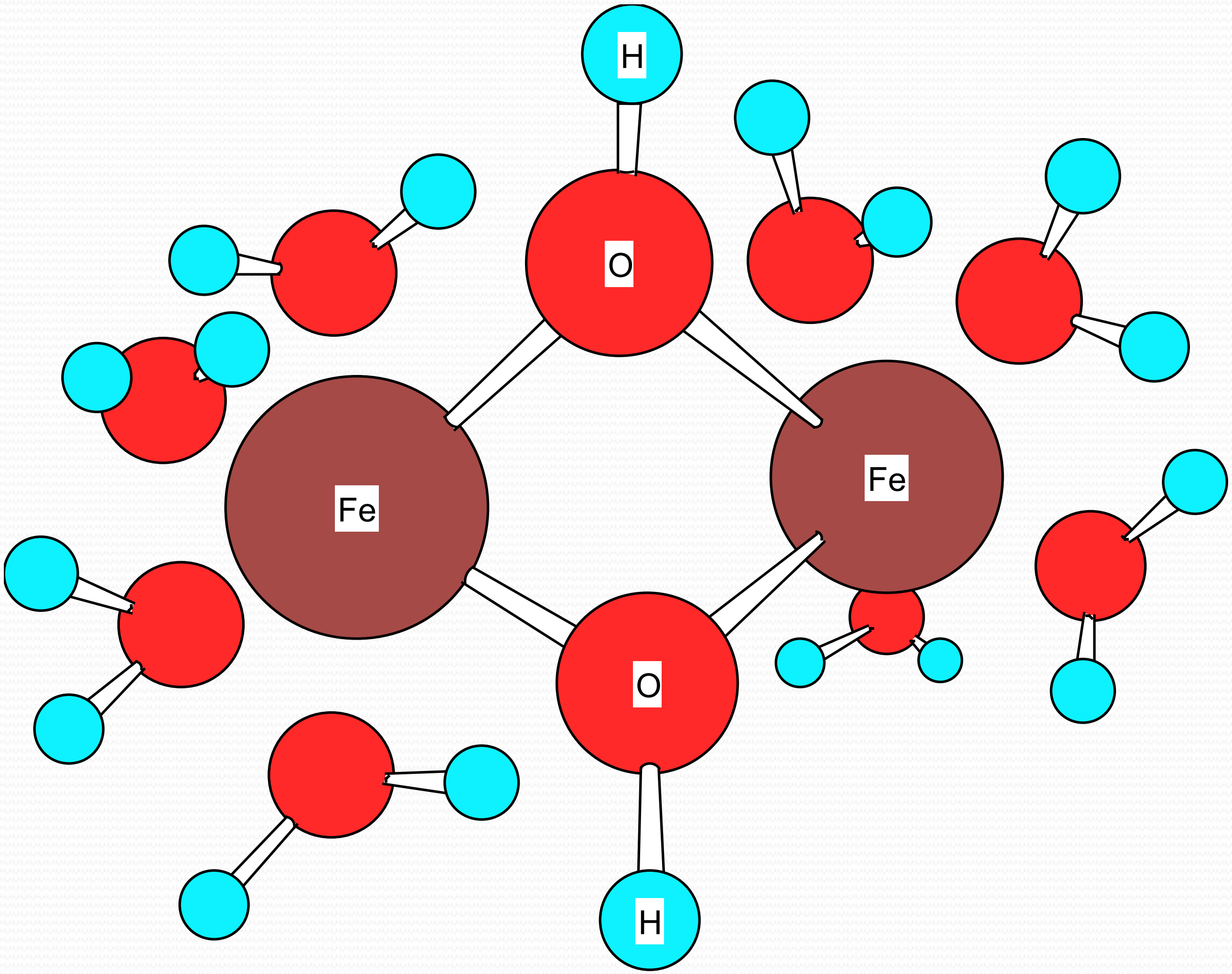
$FeOH(H_2O)_5^{+2}$



$Fe(OH)_2(H_2O)_4^+$



Dimer



Metals and acidity

- Metals increase the acidity of water
- Greater as:
  - Metal charge increases
  - Metal radius decreases
- As acidity increases, the predominant species progresses down the list
  - Aquo ion
  - Hydroxo complex
  - Hydroxy-oxo complex
  - Oxo complex

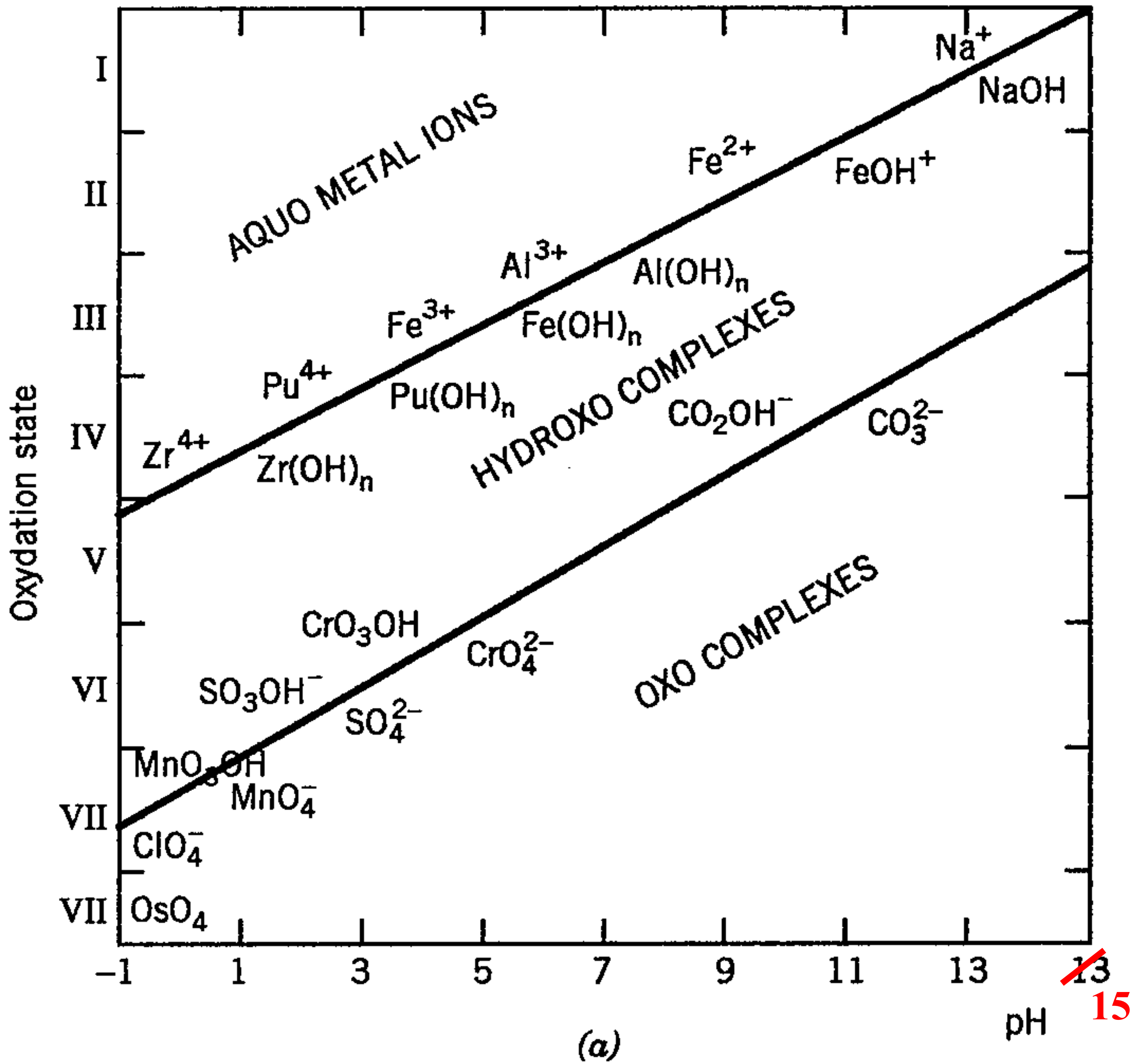


Fig 6.4a

Pg.262

$^*K_1$

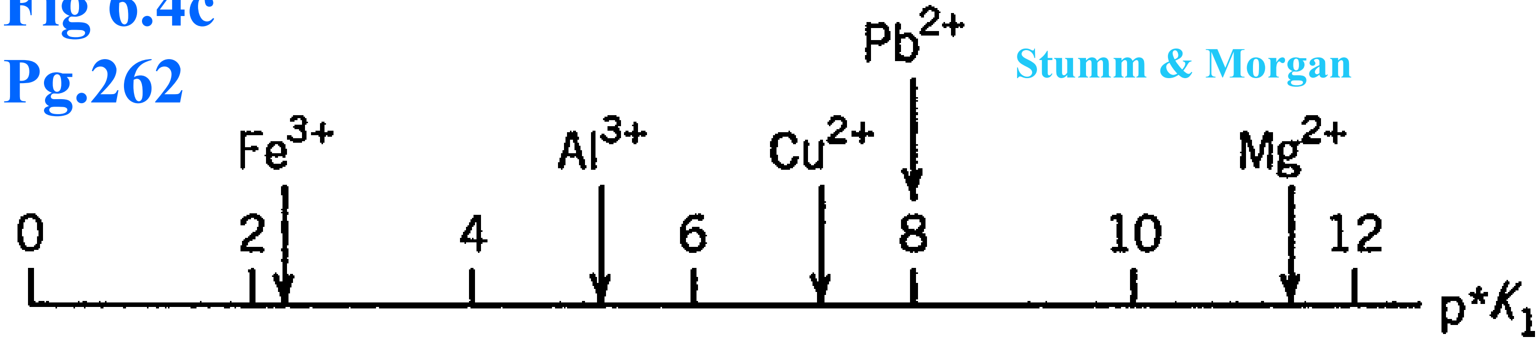
$$^*K_1 = \frac{[Zn(OH)^+][H^+]}{[Zn^{+2}]}$$

- A measure of the extent/strength of hydrolysis
  - The first hydrolysis constant pK_1 of an aqua metal ion is dependent on the ionic charge and radius of the metal ion. The pK_1 values of the aqua metal ions, studied here at 25°C follow, the order:
    - Pb (7.8) ~ Cu (8.0) < Zn (8.96) < Co (9.85) < Ni (9.86) < Ag (11.1)

Barauh et al., 2014 [J. Geochem]

Fig 6.4c
Pg.262

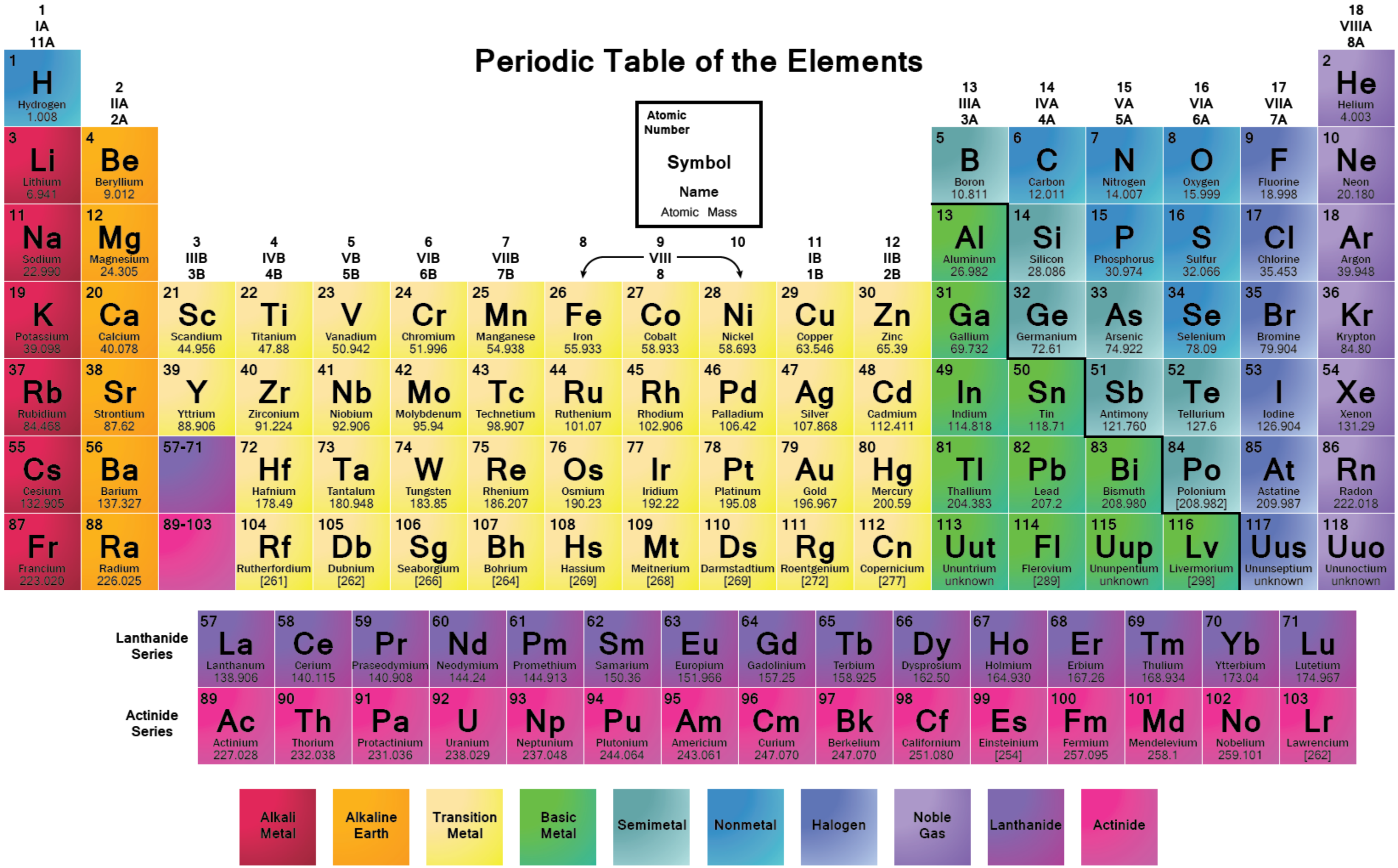
Stumm & Morgan



As pK_1 goes up strength of OH complex goes down

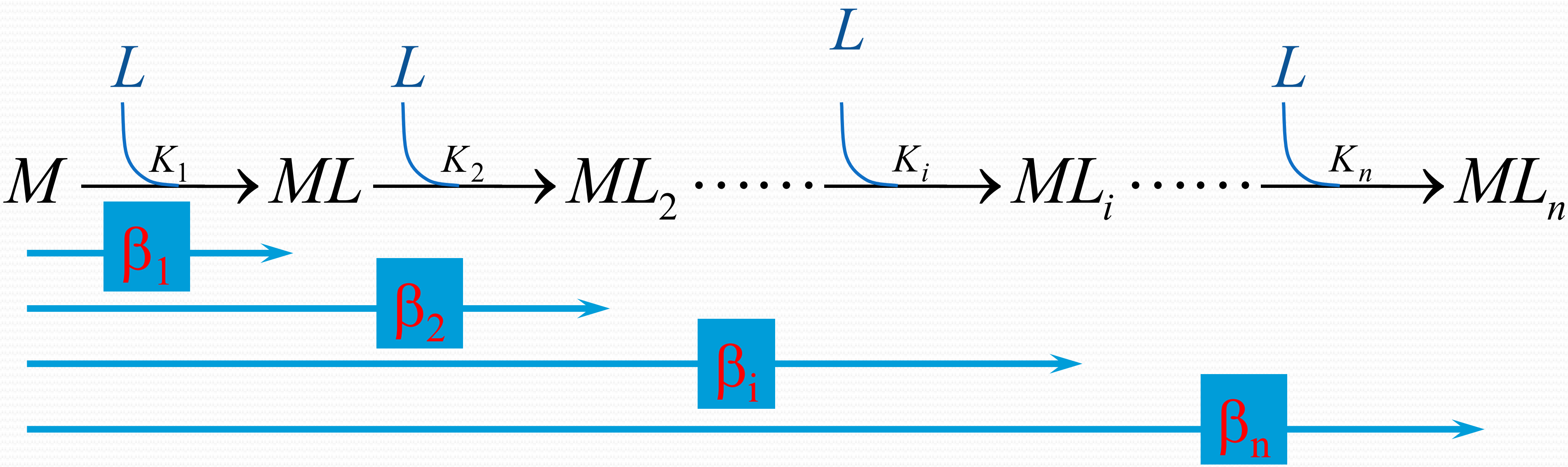
Complexation of hydroxide?

- Pb (7.8) ~ Cu (8.0) > Zn (8.96) > Co (9.85) > Ni (9.86) > Ag (11.1)



Stability Constants

- Addition of a Ligand

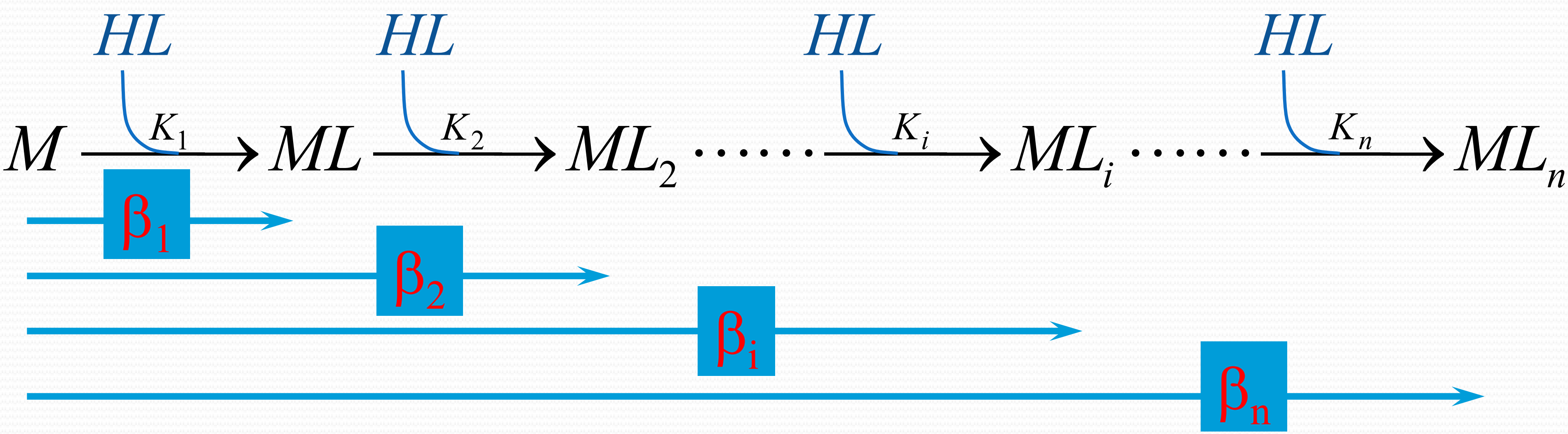


$$K_i = \frac{[ML_i]}{[ML_{(i-1)}][L]}$$

$$\beta_i = \frac{[ML_i]}{[M][L]^i}$$

Stability Constants

- Addition of protonated Ligands

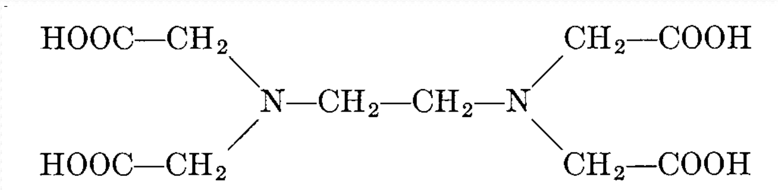


$$K_i = \frac{[ML_i][H^+]}{[ML_{(i-1)}][HL]}$$

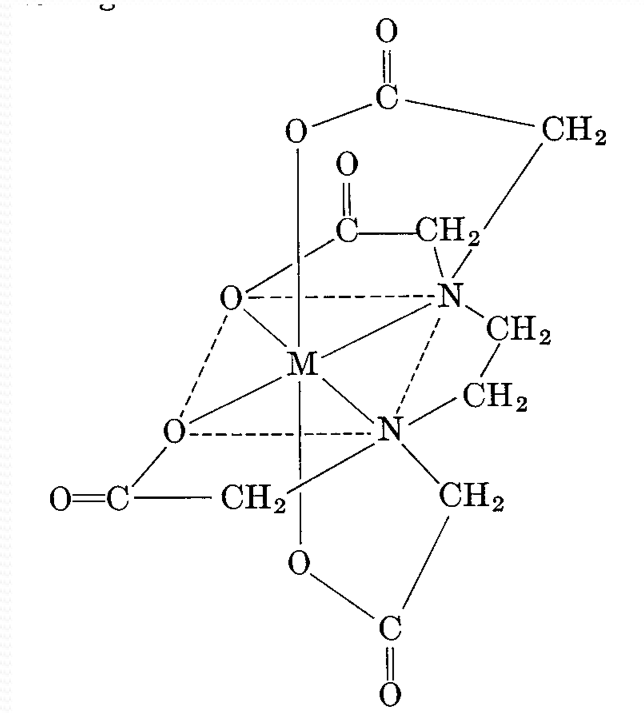
$$\beta_i = \frac{[ML_i][H^+]^i}{[M][HL]^i}$$

EDTA

- Hexadentate Ligand
  - Ethylenediamine Tetraacetic Acid
    - Free form

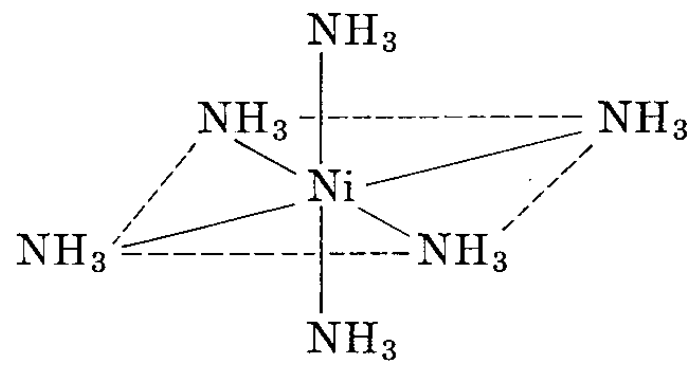


    - Interest to Env. Eng.
      - Used in pollutant analysis
      - Model for NOM
      - Used for controlling scale
        - Huang et al., 2000 [JEED 126:10:919]



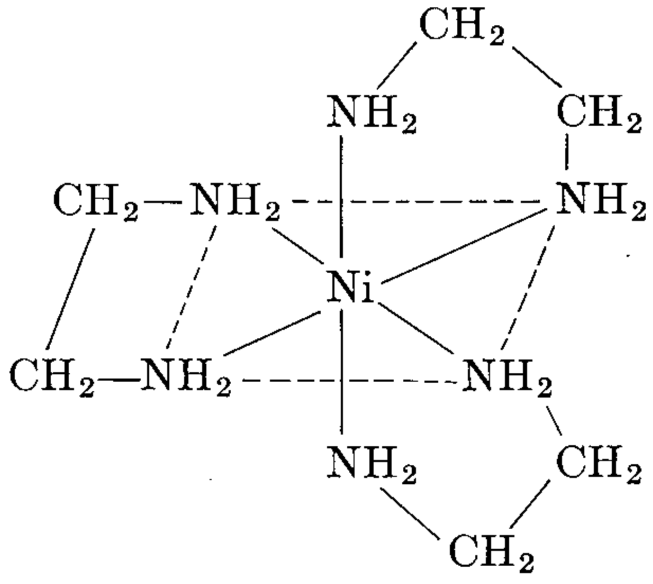
From: Butler, 1964

- Ni-hexammine

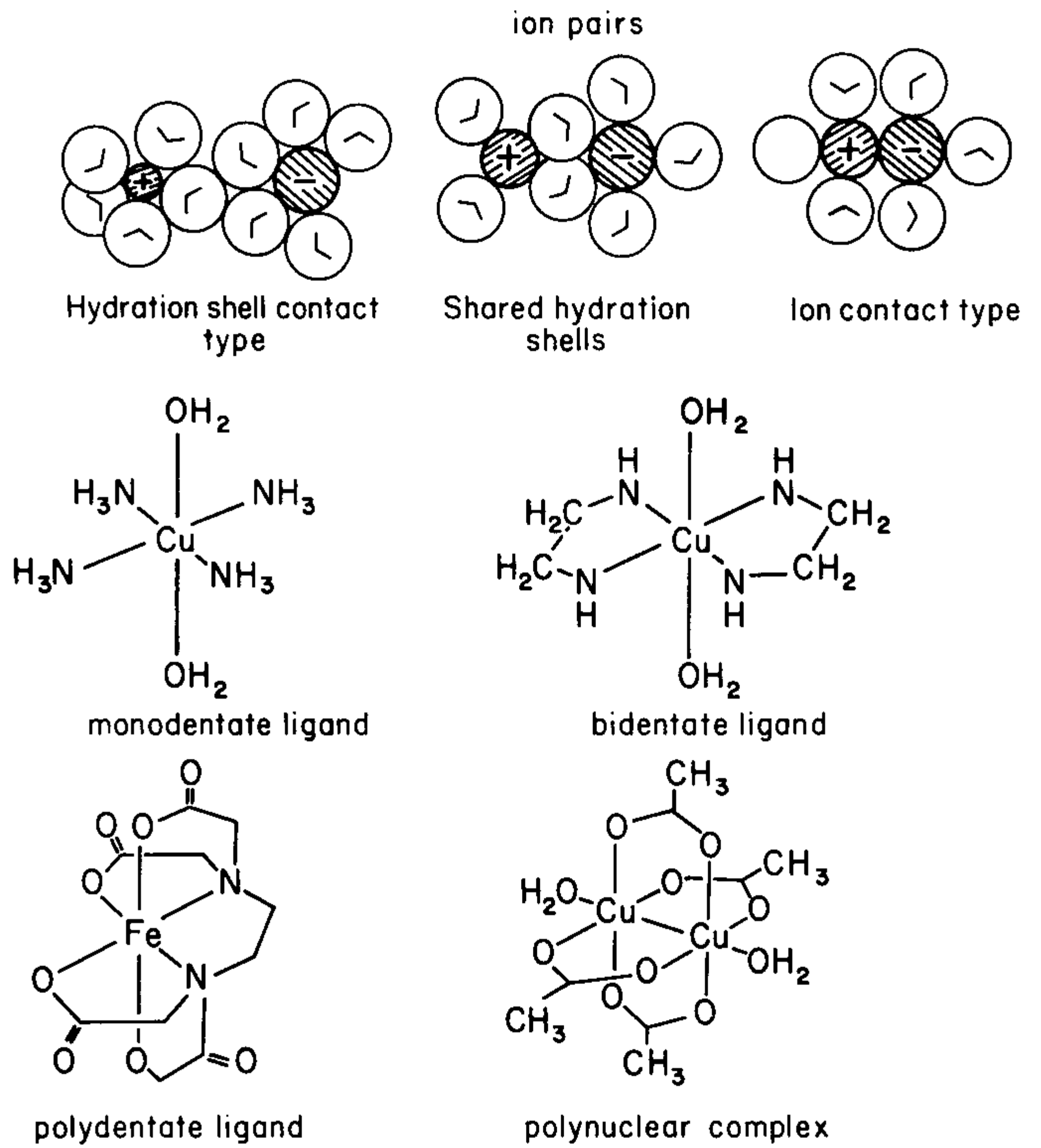


- Tris(ethylene) diamine nickel (II)

n tris(ethylene diamine) nickel (II),



Butler, 1964; pg.374



From: Morel & Hering, 1993

Development of alpha

- Recall:

$$\beta_2 = K_1 K_2 = \frac{[Zn(OH)_2]}{[Zn^{+2}][OH^-]^2}$$

$$\beta_i = \frac{[ML_i]}{[M][L]^i}$$

- So:

$$\beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$\frac{[ML_2]}{[M]} = \beta_2 [L]^2$$

and

$$\beta_3 = \frac{[ML_3]}{[M][L]^3}$$

$$\frac{[ML_3]}{[M]} = \beta_3 [L]^3$$

Etc.

Alpha (cont.)

- Now let's define, and alpha value
  - And $\alpha_0 \equiv \frac{[M]}{C_M} = \frac{[M]}{[M]+[ML]+[ML_2]+\cdots+[ML_n]}$

$$\alpha_0 \equiv \frac{[M]}{C_M} = \left(\frac{[M]+[ML]+[ML_2]+\cdots+[ML_n]}{[M]}\right)^{-1}$$

$$= \left(\frac{[M]}{[M]} + \frac{[ML]}{[M]} + \frac{[ML_2]}{[M]} + \cdots + \frac{[ML_n]}{[M]}\right)^{-1}$$

$$= \left(1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_n[L]^n\right)^{-1}$$

$$\beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$\frac{[ML_2]}{[M]} = \beta_2[L]^2$$

Alpha (cont.)

- Now other alpha's can be determined
  - And

$$\alpha_1 \equiv \frac{[ML]}{C_M} = \frac{[M]}{C_M}\frac{[ML]}{[M]} = \alpha_0 \beta_1 [L]$$

$$\beta_1 = \frac{[ML]}{[M][L]}$$

$$\frac{[ML]}{[M]} = \beta_1 [L]$$

$$\alpha_2 \equiv \frac{[ML_2]}{C_M} = \frac{[M]}{C_M}\frac{[ML_2]}{[M]} = \alpha_0 \beta_2 [L]^2$$

$$\beta_2 = \frac{[ML_2]}{[M][L]^2}$$

$$\frac{[ML_2]}{[M]} = \beta_2 [L]^2$$

  - So in general

$$\alpha_n \equiv \frac{[ML_n]}{C_M} = \alpha_0 \beta_n [L]^n$$

Summary

- In summary:

$$\alpha_0 \equiv \frac{[M]}{C_M} = \left(1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_n[L]^n\right)^{-1}$$

$$\alpha_n \equiv \frac{[ML_n]}{C_M} = \alpha_0 \beta_n [L]^n$$

  - So if we know [L] and the β's we can determine the entire speciation of the metal
  - This is analogous to the α's of the acid/base systems
    - Where if you know $[H^+]$ and the α's , you can determine the entire acid/base speciation

- To next lecture

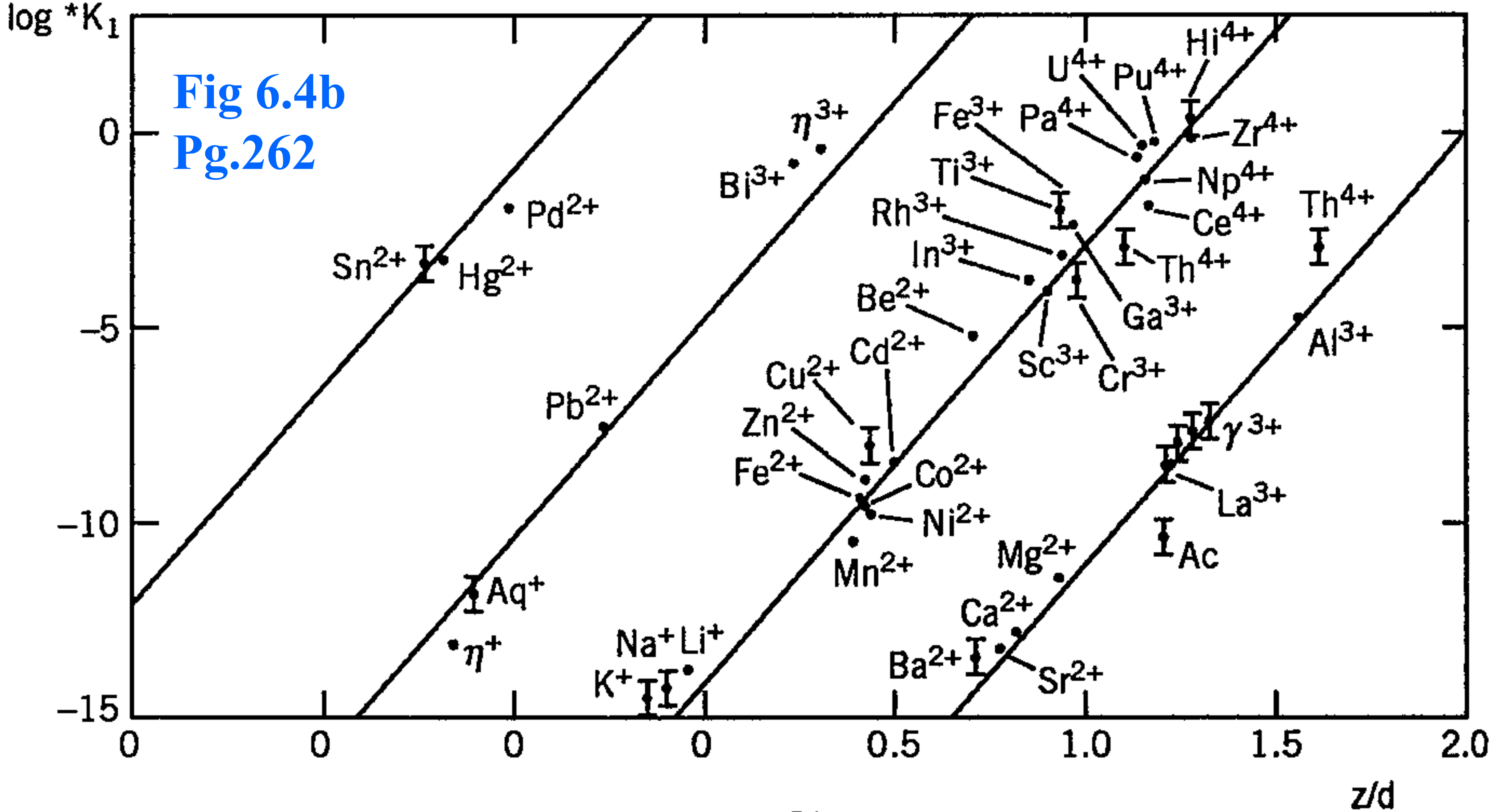


Fig 6.4b
Pg.262
log *K1
0
−5
−10
−15
0
0
0
0
0.5
1.0
1.5
2.0
z/d
Sn2+
Hg2+
Pd2+
Aq+
η+
Pb2+
Bi3+
η3+
Na+
Li+
K+
Cu2+
Cd2+
Zn2+
Fe2+
Co2+
Ni2+
Mn2+
Be2+
In3+
Rh3+
Ti3+
Fe3+
Pa4+
U4+
Pu4+
Hi4+
Zr4+
Np4+
Ce4+
Th4+
Ga3+
Sc3+
Cr3+
Th4+
Al3+
γ3+
La3+
Ac
Mg2+
Ca2+
Ba2+
Sr2+

(b)