

CEE 680: Water Chemistry

Lecture #28

Coordination Chemistry: Hydrolysis and Simple Complexes

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

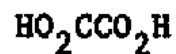
Benjamin; Chapter 8.1-8.6

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

C ₂ H ₂ O ₄ Metal ion	Equilibrium	Ethanedioic acid (oxalic acid)			ΔH 25°, 0	ΔS 25°, 0
		Log K 25°, 0.1	Log K 25°, 1.0	Log K 25°, 0		
H ⁺	HL/H.L	3.82 ± 0.04	3.55 ± 0.02	4.266 ± 0.001	1.60 ± 0.06	25.1
	H ₂ L/HL.H	1.04 ± 0.10	1.04 ± 0.04	1.252	0.9 ± 0.1	18.0 ^c
K ⁺	ML/M.L					-0.8 ⁿ
Ba 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			
Sr ²⁺	MHL/M.HL	1.38				1.84
	M(HL) ₂ /M.(HL) ²	1.8				
	ML/M.L		1.25			2.54 ⁿ
	ML ₂ /M.L ²		1.90			
	MHL/M.HL	1.11				1.57
Ba ²⁺	M(HL) ₂ /M.(HL) ²	1.7				
	ML/M.L					2.31 ⁿ
Sc ³⁺	ML/M.L					
	ML ₂ /M.L ²	8.74 ^x				
	ML ₂ /M.L ²		6.86 ^j			
	ML ₂ /M.L ³		11.31 ^j			
	ML ₃ /M.L ⁴		14.32 ^j			
Y ³⁺	ML ₄ /M.L ⁴		16.70 ^j			
	MHL/M.HL	7.36 ^x				
	ML/M.L	5.46				
La ³⁺	ML ₂ /M.L ²	9.29				
	ML/M.L	4.71	4.3			
Ce ³⁺	ML ₂ /M.L ²	7.83	7.9			
	ML ₃ /M.L ³		10.3			
	ML/M.L	4.90	4.49 ^j			6.52
Ce ³⁺	ML ₂ /M.L ²	8.26	7.91 ^j			10.48
	ML ₂ /M.L ³		10.30 ^j			11.30
	ML ₃ /M.L ⁴		11.75 ^j			
	ML ₄ /M.L ⁴					
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 ±0.0			
	ML ₂ /M.L ³		11.45 ^j -0.2			
	ML ₃ /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; ^x 25°, 0.05



C ₂ H ₂ O ₄ Metal ion	Equilibrium	Ethanedioic acid (oxalic acid)			ΔH 25°, 0	H ₂ L ΔS 25°, 0
		Log K 25°, 0.1	Log K 25°, 1.0	Log K 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 ₂ L/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			

Sources: Stumm & Morgan, 3rd Ed.

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 ₂ L ₄	42.1				AlL ₄	19.1							
	AlL ₃ ·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 ₂ L ₂	25.0												
	FeL ₃ ·s	42.7												
	FeL ₃ ·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·s	10.4								MnL ₂	1.5	
	MnL ₃	7.2												
	MnL ₄	7.7												
	MnL ₂ ·s	12.8												
	Fe ²⁺	FeL	4.5	FeL·s	10.7	FeL	2.2				FeL	1.4		
FeL ₂		7.4												
FeL ₃		11.0												
FeL ₂ ·s		15.1												
Co ²⁺	CoL	4.3	CoL·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 ·s	15.7											CoL ₄	5.0
Ni ²⁺	NiL	4.1	NiL·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 ₄	17.2											NiL ₄	7.7

• Pg. 326

• From Morel & Hering, 1993

Sources: Stumm & Morgan, 2nd Ed.

• Pg. 242

242 TABLE 5.1 (continued)

	Symbol for Equilibrium Constants	log K at 25°C	I
$\alpha\text{-Al(OH)}_3(\text{s}) + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$	* K_{s0}	8.5	0
$\text{Al(OH)}_3(\text{amorph}) + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$	* K_{s0}	10.8	0
$\text{CuO}(\text{s}) + 2\text{H}^+ = \text{Cu}^{2+} + \text{H}_2\text{O}$	* K_{s0}	7.65	0
$\text{Cu}^{2+} + \text{OH}^- = \text{CuOH}^+$	K_1	6.0 (18°C)	0
$\text{Cu}^{2+} + 2\text{OH}^- = \text{Cu(OH)}_2$	K_2	12.8	1
$2\text{Cu}^{2+} + 2\text{OH}^- = \text{Cu}_2(\text{OH})_2^{2+}$	$K_{2,2}$	17.0 (18°C)	0
$\text{Cu}^{2+} + 3\text{OH}^- = \text{Cu(OH)}_3^-$	K_3	15.2	0
$\text{Cu}^{2+} + 4\text{OH}^- = \text{Cu(OH)}_4^{2-}$	K_4	16.1	0
$\text{Zn}^{2+} + \text{H}_2\text{O} = \text{ZnOH}^+ + \text{H}^+$	* K_1	- 8.96	0
$\text{Zn}^{2+} + 2\text{H}_2\text{O} = \text{Zn(OH)}_2 + 2\text{H}^+$	* β_2	- 16.9	0
$\text{Zn}^{2+} + 3\text{H}_2\text{O} = \text{Zn(OH)}_3^- + 3\text{H}^+$	* β_3	- 28.4	0
$\text{Zn}^{2+} + 4\text{H}_2\text{O} = \text{Zn(OH)}_4^{2-} + 4\text{H}^+$	* β_4	- 41.2	0
$\text{ZnO} + 2\text{H}^+ = \text{Zn}^{2+} + \text{H}_2\text{O}$	* K_{s0}	11.14	0
$\text{Zn(OH)}_2(\text{amorph}) + 2\text{H}^+ = \text{Zn}^{2+} + 2\text{H}_2\text{O}$	* K_{s0}	12.45	0
$\text{Cd}^{2+} + \text{H}_2\text{O} = \text{CdOH}^+ + \text{H}^+$	* K_1	- 10.1	0
$\text{Cd}^{2+} + 2\text{H}_2\text{O} = \text{Cd(OH)}_2(\text{aq}) + 2\text{H}^+$	* β_2	- 20.4	0
$\text{Cd}^{2+} + 3\text{H}_2\text{O} = \text{Cd(OH)}_3^- + 3\text{H}^+$	* β_3	< - 33.3	0
$\text{Cd}^{2+} + 4\text{H}_2\text{O} = \text{Cd(OH)}_4^{2-} + 4\text{H}^+$	* β_4	- 47.4	0

Reconciling the constants: $\text{Al}(\text{OH})_3$

- S&M:3rd Edition

- $\text{AlL}_3 \text{ s} \quad 10^{33.5}$

$$\frac{\text{AlL}_3(\text{s})}{\text{Al} \cdot \text{L}^3} = 10^{33.5}$$

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

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

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

- S&M:2nd Edition

- $\alpha\text{-Al}(\text{OH})_3(\text{s}) + 3\text{H}^+ = \text{Al}^{+3} + 3\text{H}_2\text{O}$

- $^*K_{\text{so}} \quad 8.5$

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

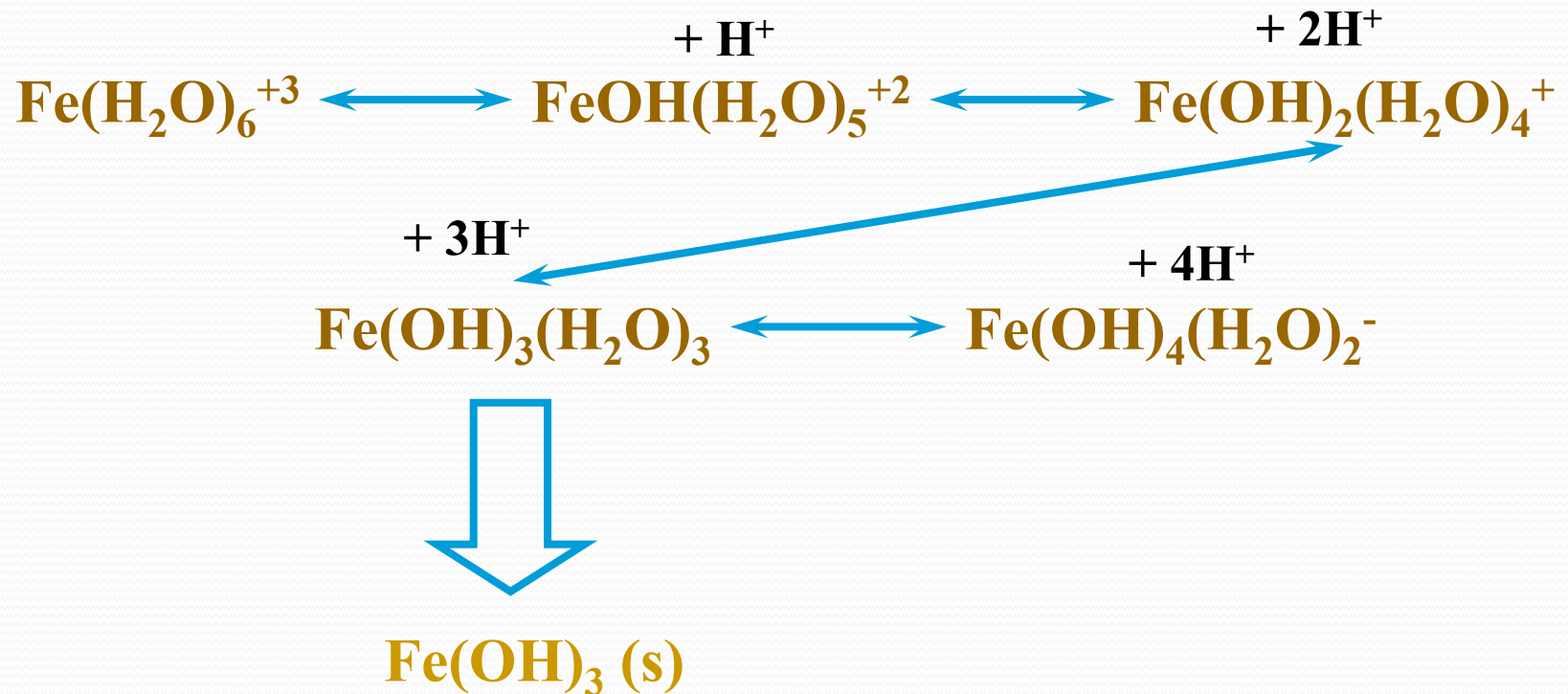
$$[\text{Al}^{+3}] = 10^{8.5} [\text{H}^+]^3$$

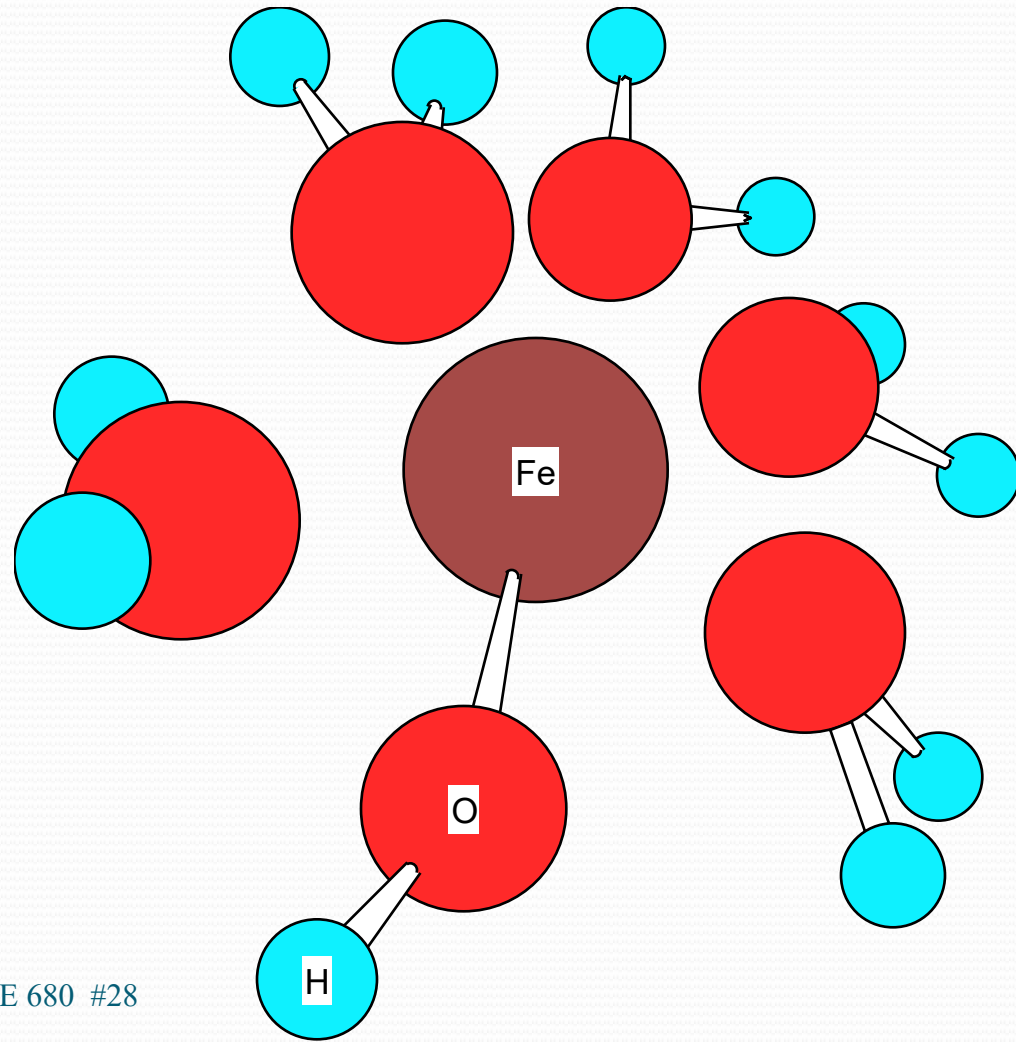
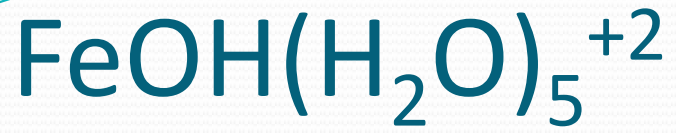
$$\log[\text{Al}^{+3}] = 8.5 - 3\text{pH}$$

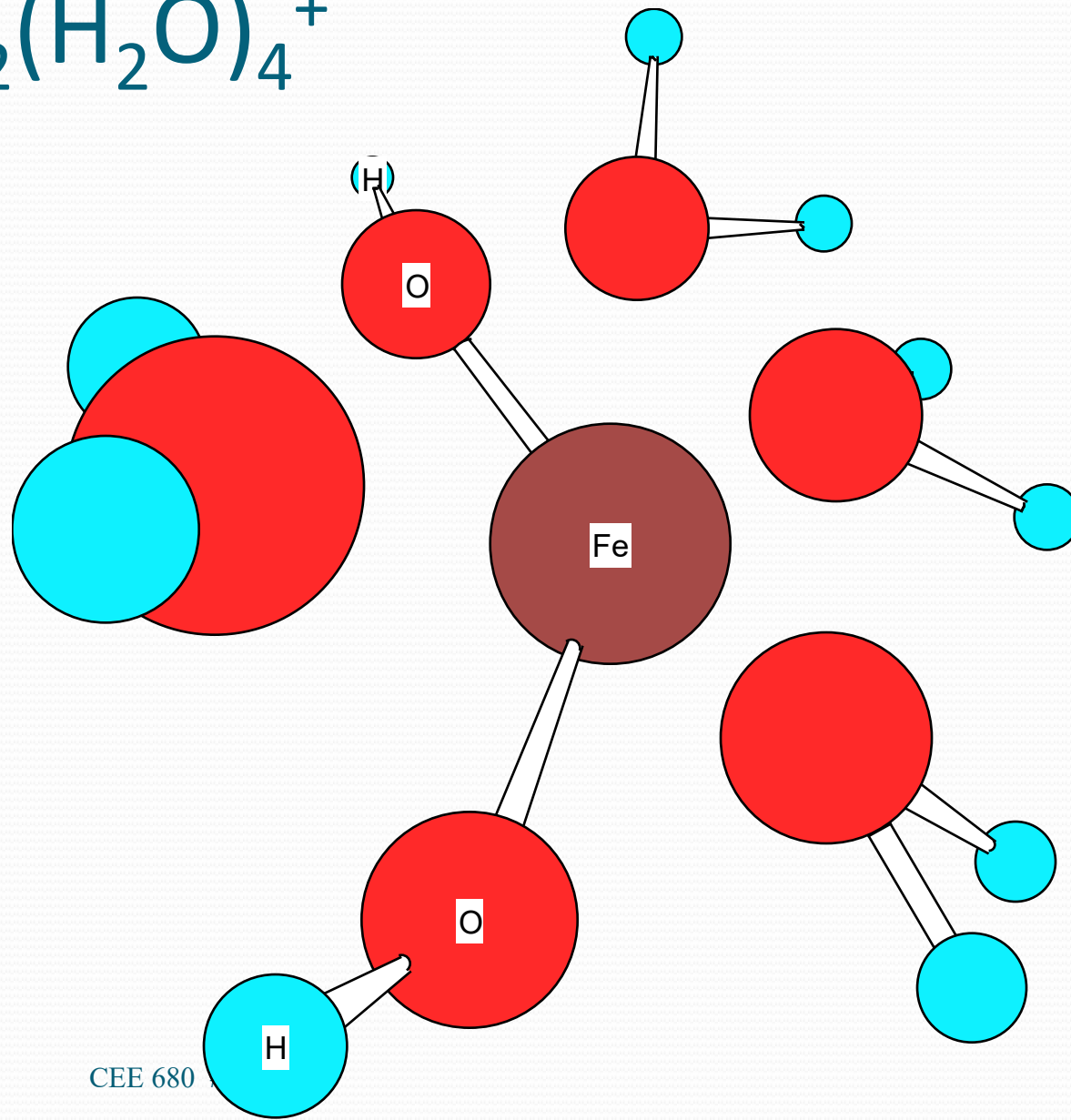
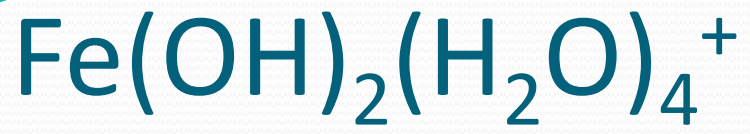


Metal Hydrolysis

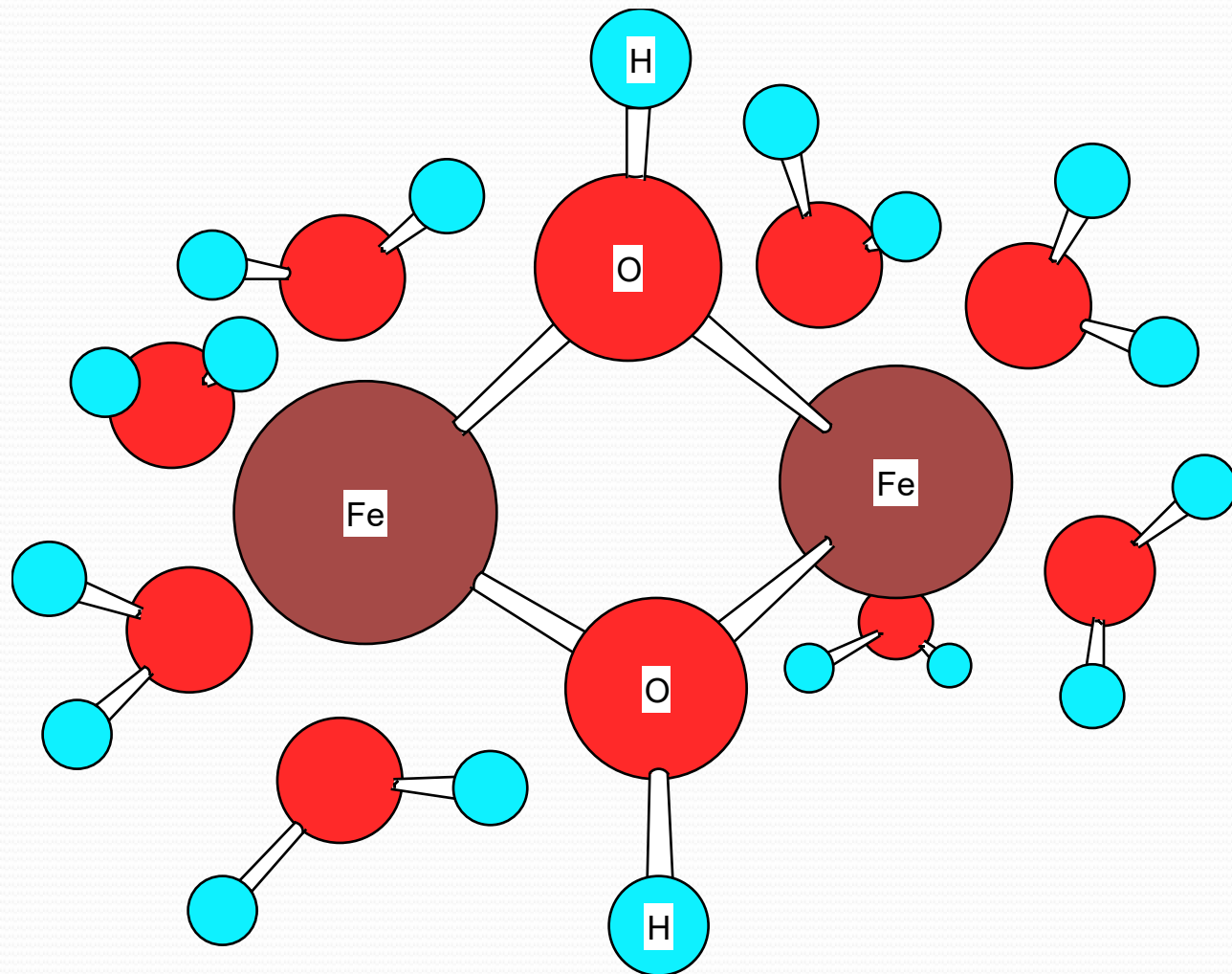
- Case for iron







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

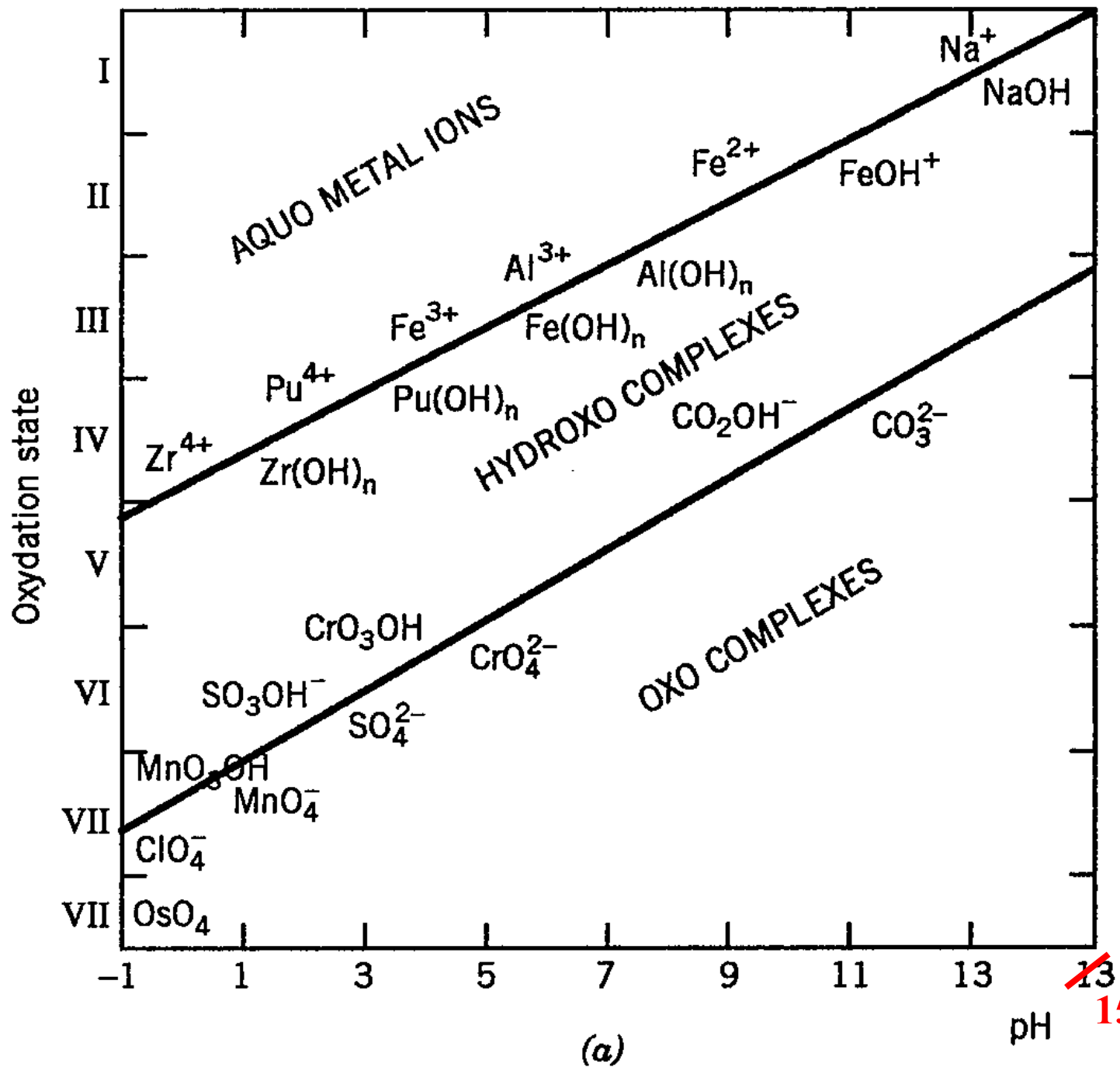


Fig 6.4a

Pg.262

David Reckhow

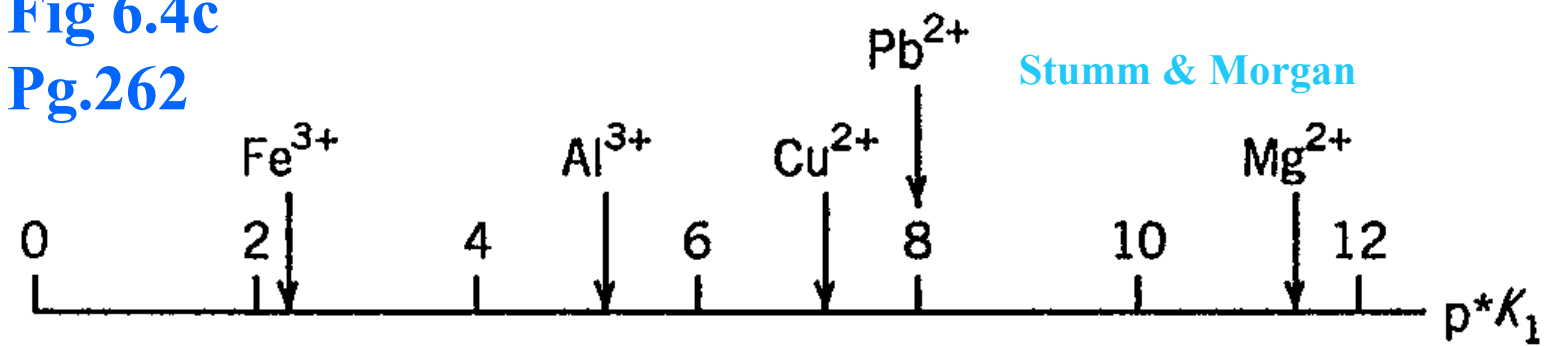
*K₁

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

- A measure of the extent/strength of hydrolysis
 - The first hydrolysis constant pK₁ of an aqua metal ion is dependent on the ionic charge and radius of the metal ion. The pK₁ 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



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)

Periodic Table of the Elements

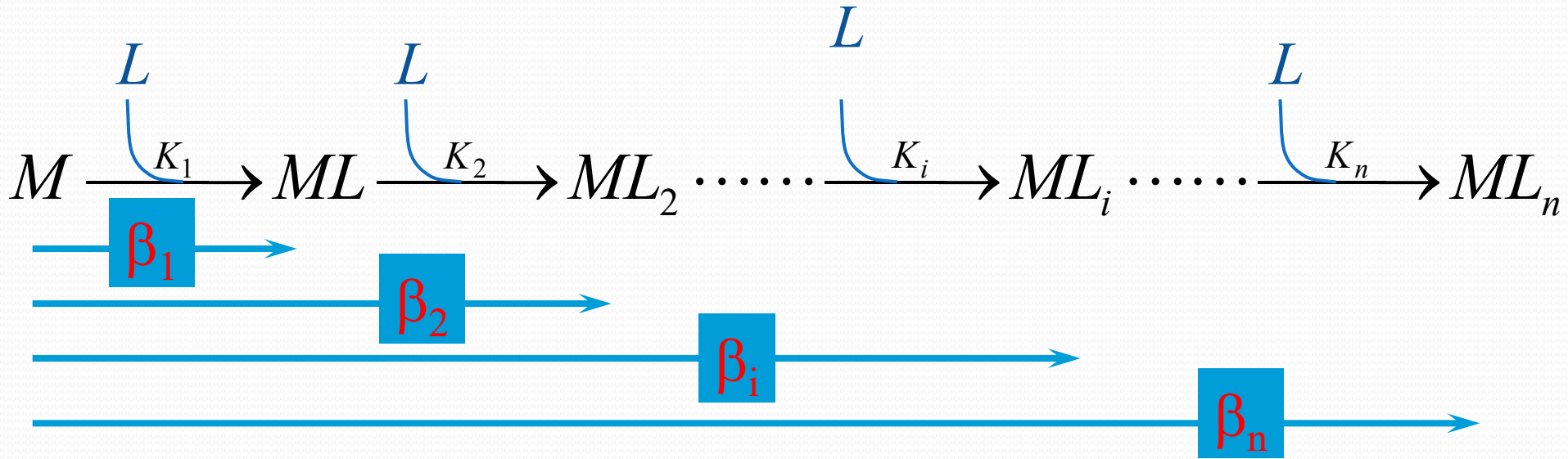
1 IA 11A																	18 VIII A 8A
1 H Hydrogen 1.008	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.09	35 Br Bromine 79.904	36 Kr Krypton 84.80
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series	57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide
--------------	----------------	------------------	-------------	-----------	----------	---------	-----------	------------	----------

Stability Constants

- Addition of a Ligand

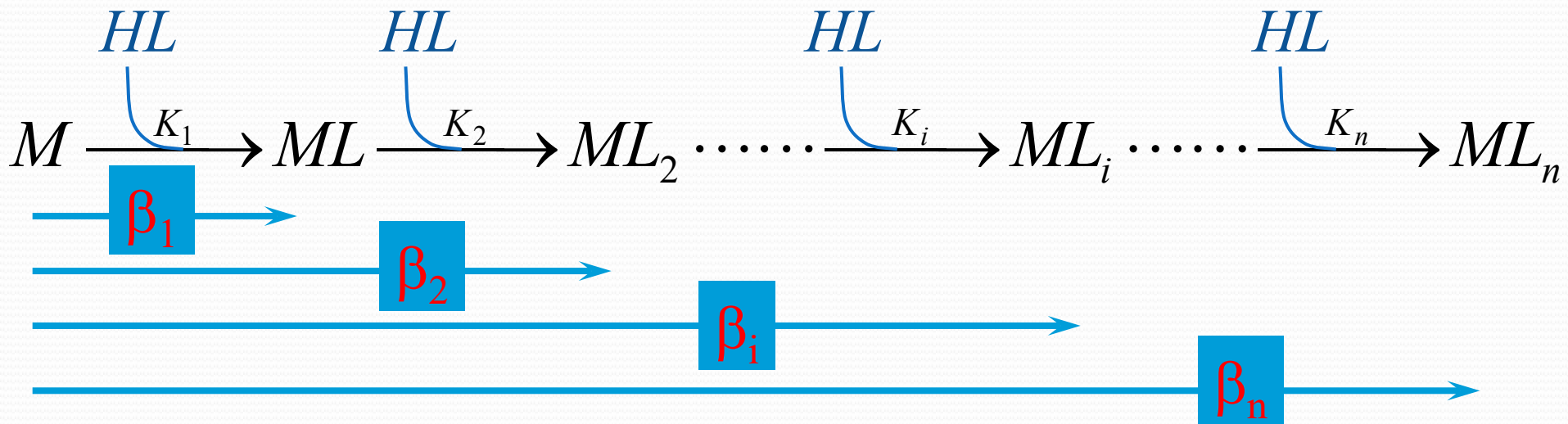


$$K_i = \frac{[ML_i]}{[ML_{(i-1)}][L]}$$

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

Stability Constants

- Addition of protonated Ligands

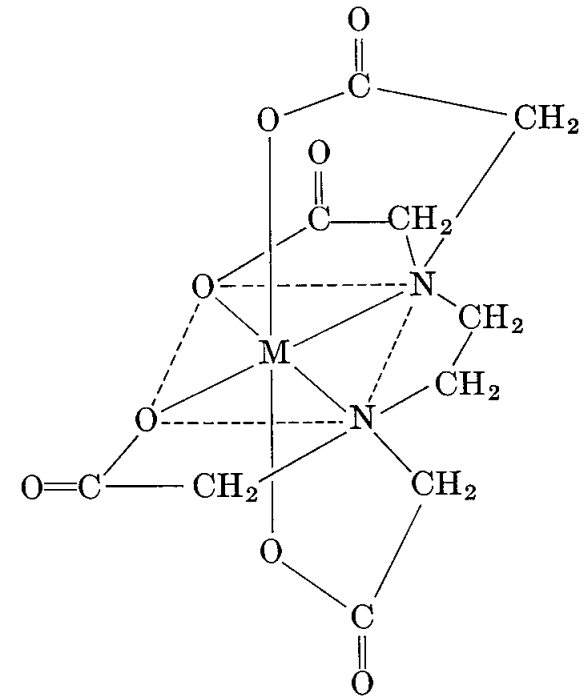
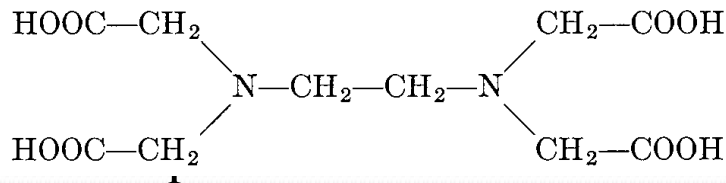


$$K_i = \frac{[ML_i][H^+]}{[ML_{(i-1)}][HL]}$$

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

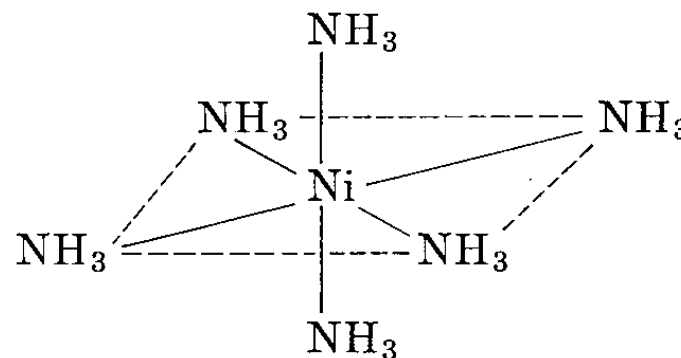
EDTA

- 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]



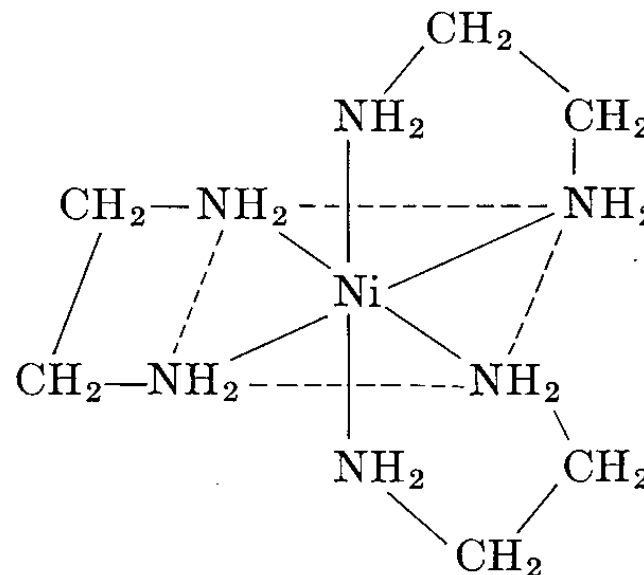
From: Butler, 1964

- Ni-hexammine

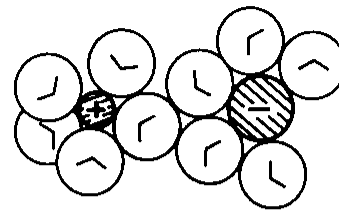


- Tris(ethylene) diamine nickel (II)

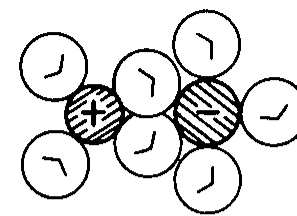
n tris(ethylene diamine) nickel (II),



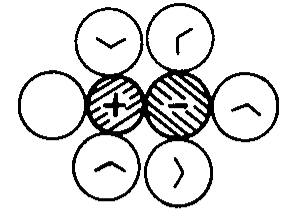
Butler, 1964; pg.374



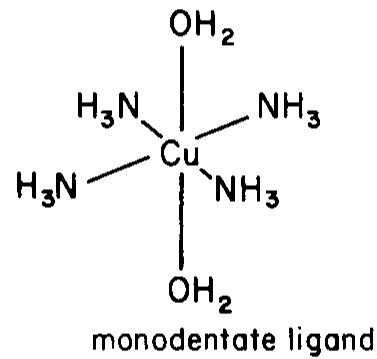
Hydration shell contact type



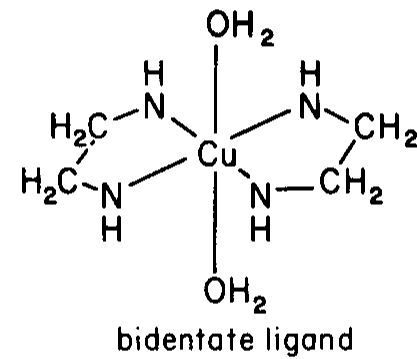
Shared hydration shells



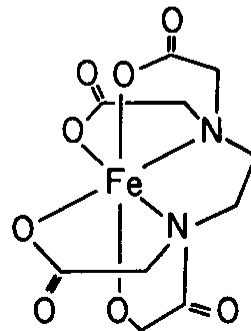
Ion contact type



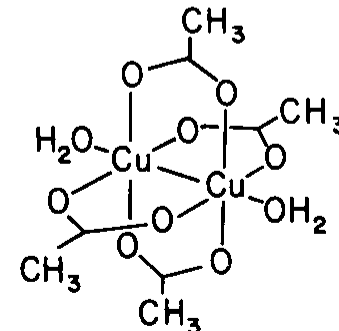
monodentate ligand



bidentate ligand



polydentate ligand



polynuclear complex

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 $\alpha_0 \equiv \frac{[M]}{C_M} = \frac{[M]}{[M] + [ML] + [ML_2] + \dots + [ML_n]}$

$$\begin{aligned}\alpha_0 &\equiv \frac{[M]}{C_M} = \left(\frac{[M] + [ML] + [ML_2] + \dots + [ML_n]}{[M]} \right)^{-1} \\ &= \left(\frac{[M]}{[M]} + \frac{[ML]}{[M]} + \frac{[ML_2]}{[M]} + \dots + \frac{[ML_n]}{[M]} \right)^{-1} \\ &= \left(1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n \right)^{-1}\end{aligned}$$

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

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

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

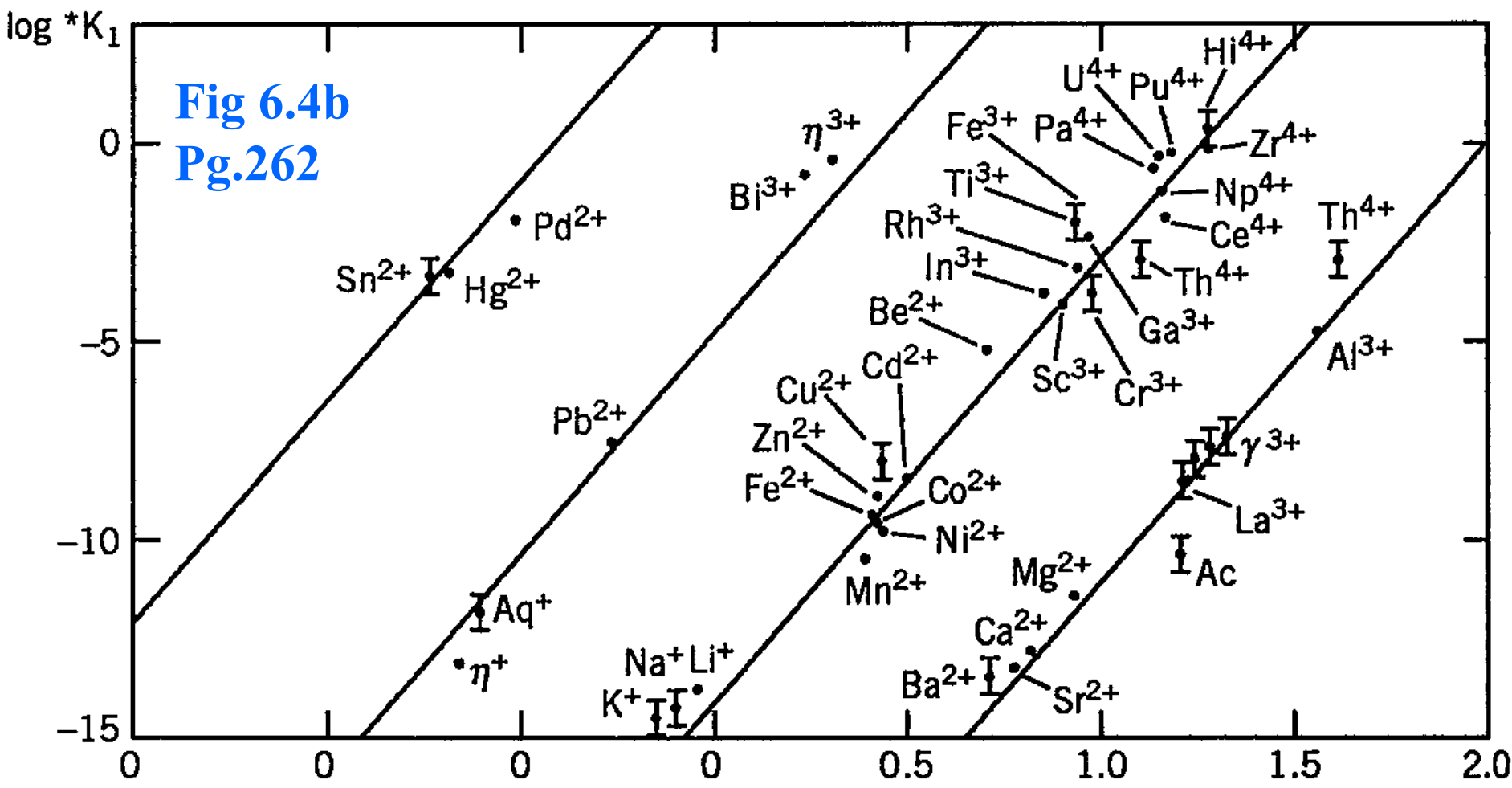


Fig 6.4b
Pg.262

(b)

z/d