

CEE 680: Water Chemistry

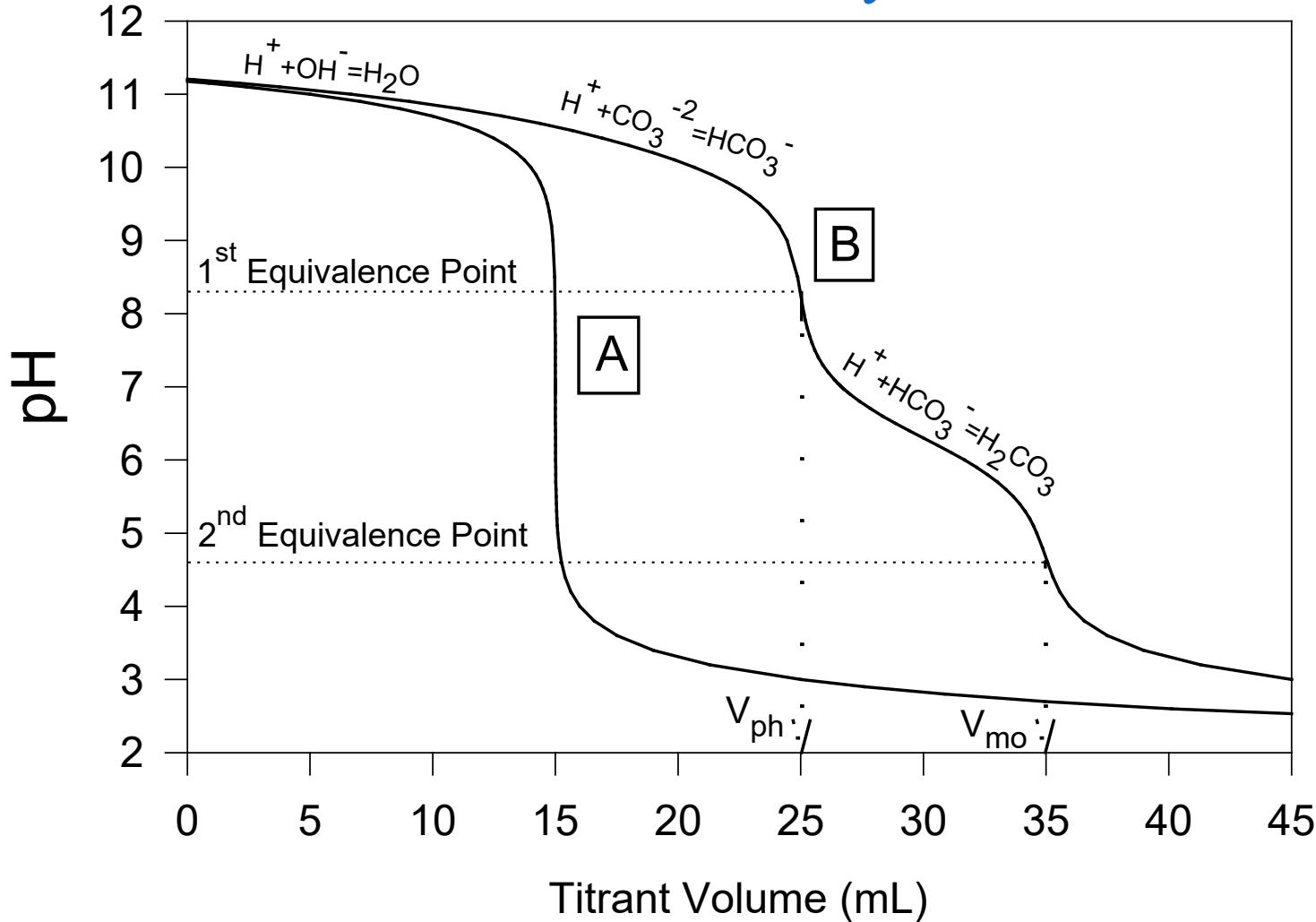
Lecture #26

Coordination Chemistry: Hydrolysis

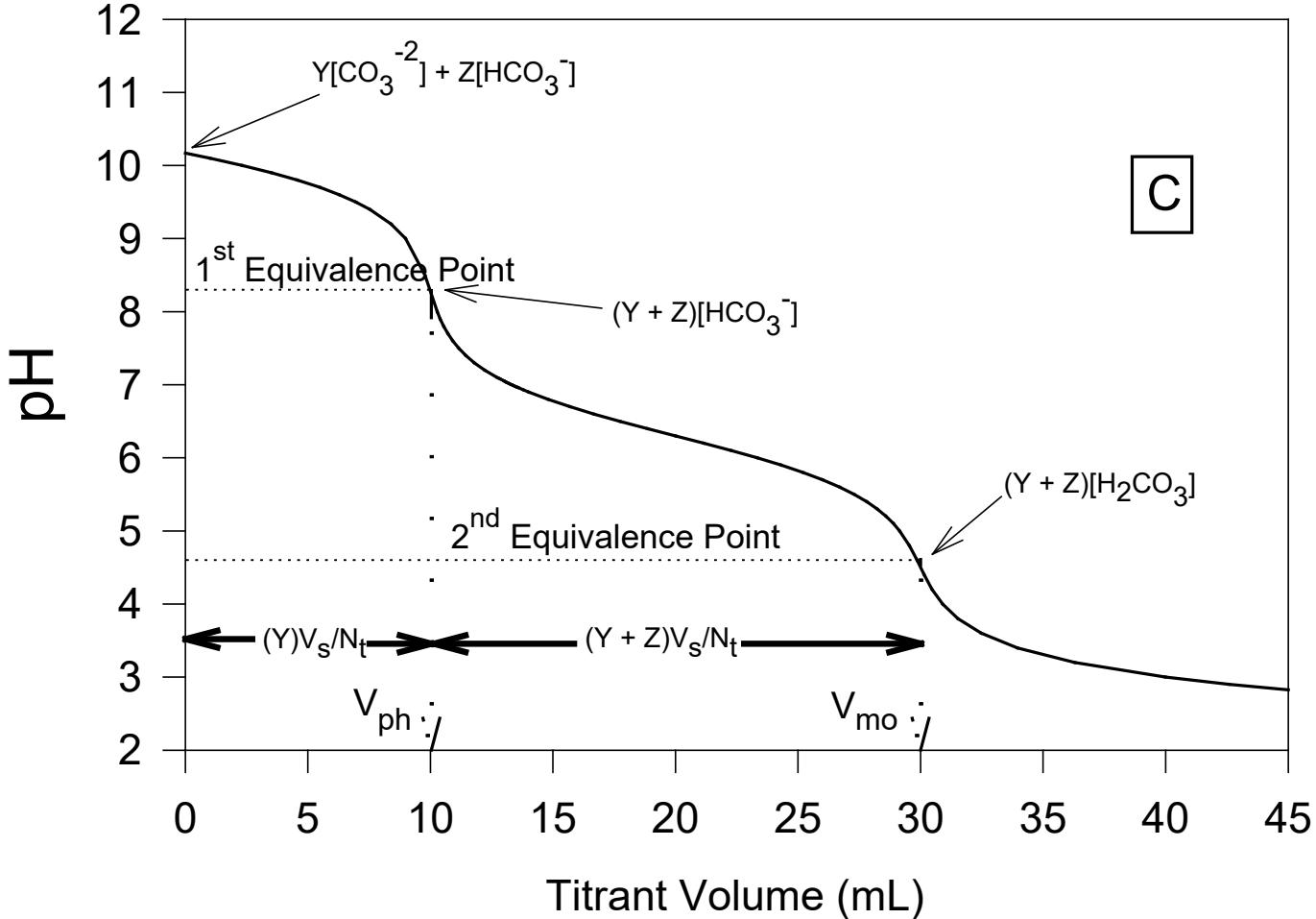
(Stumm & Morgan, Chapt.6: pg.260-271)

Benjamin; Chapter 8.1-8.6

Acid Titration Curve for a Water Containing Hydroxide and Carbonate Alkalinity



Acid Titration Curve for a Water Containing Carbonate and Bicarbonate Alkalinity

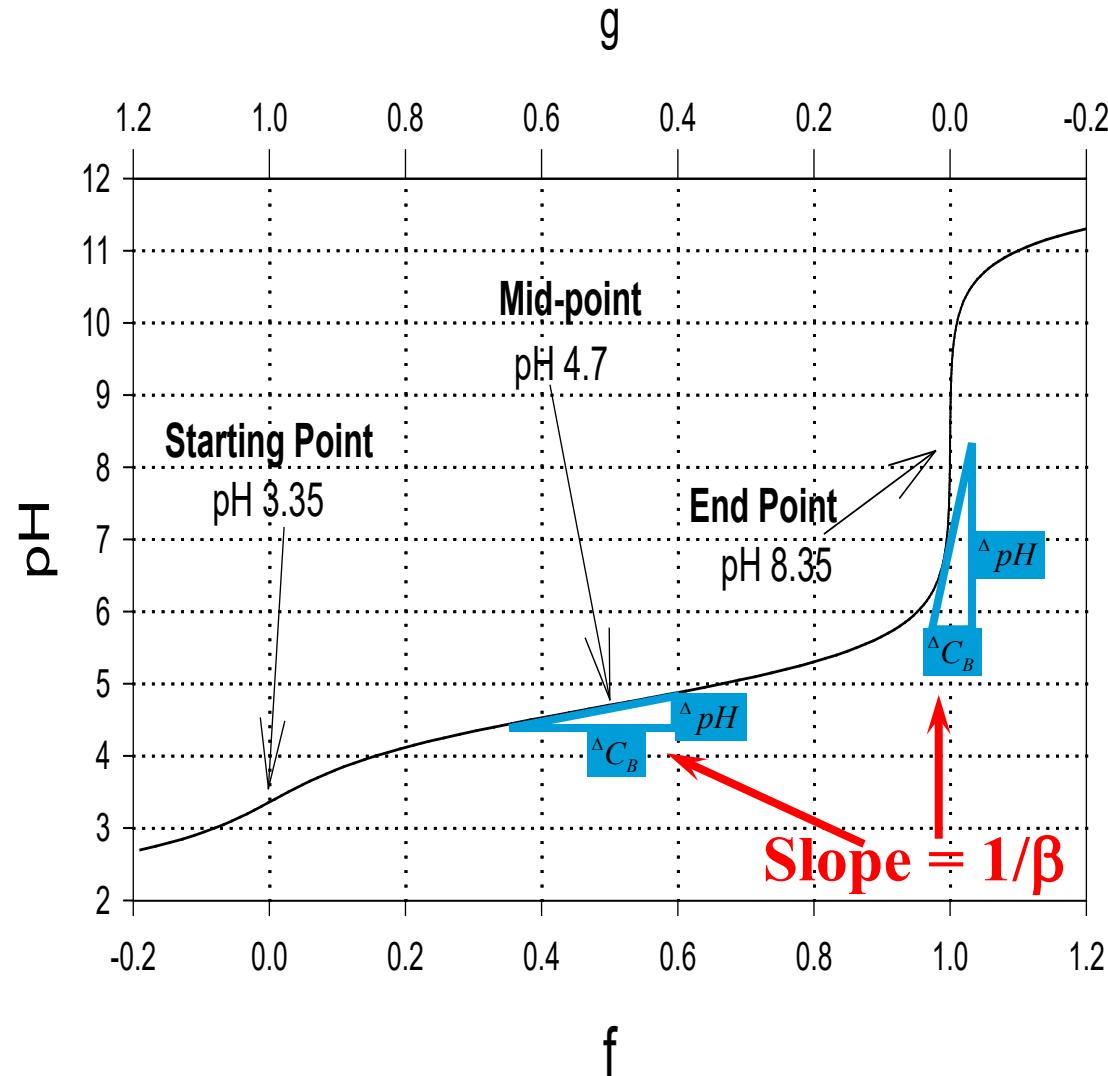


Buffer Intensity

- Amount of strong acid or base required to cause a specific small shift in pH

$$\beta = \frac{dC_B}{dpH} = -\frac{dC_A}{dpH}$$

10^{-2}M HAc



Base titration of an acid

- For a monoprotic
 - Lecture #16
 - $C_B \equiv [Na^+] = [A^-] + [OH^-] - [H^+]$

$$f = \frac{V_B N_B}{V_s M_s} = \frac{equ_B}{moles_s} = \frac{C_B}{C_T}$$
$$= \frac{[A^-] + [OH^-] - [H^+]}{C_T}$$

$$= \alpha_1 + \frac{[OH^-] - [H^+]}{C_T}$$



$$\frac{1}{\frac{[H^+]}{K_a} + 1}$$

- For a diprotic
 - Using the same ENE approach

$$f = \frac{2[A^{-2}] + [HA^-] + [OH^-] + [H^+]}{C_T}$$

$$f = 2\alpha_2 + \alpha_1 + \frac{[OH^-] + [H^+]}{C_T}$$



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

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

Example Titration

- Base titration
 - $V_s = 1000 \text{ mL}$
 - $M_s = 0.001 \text{ M}$
 - $N_B = 0.1 \text{ M}$
- Starting acids
 - Pure water
 - 1 mM HAc
 - 1 mM H_2CO_3

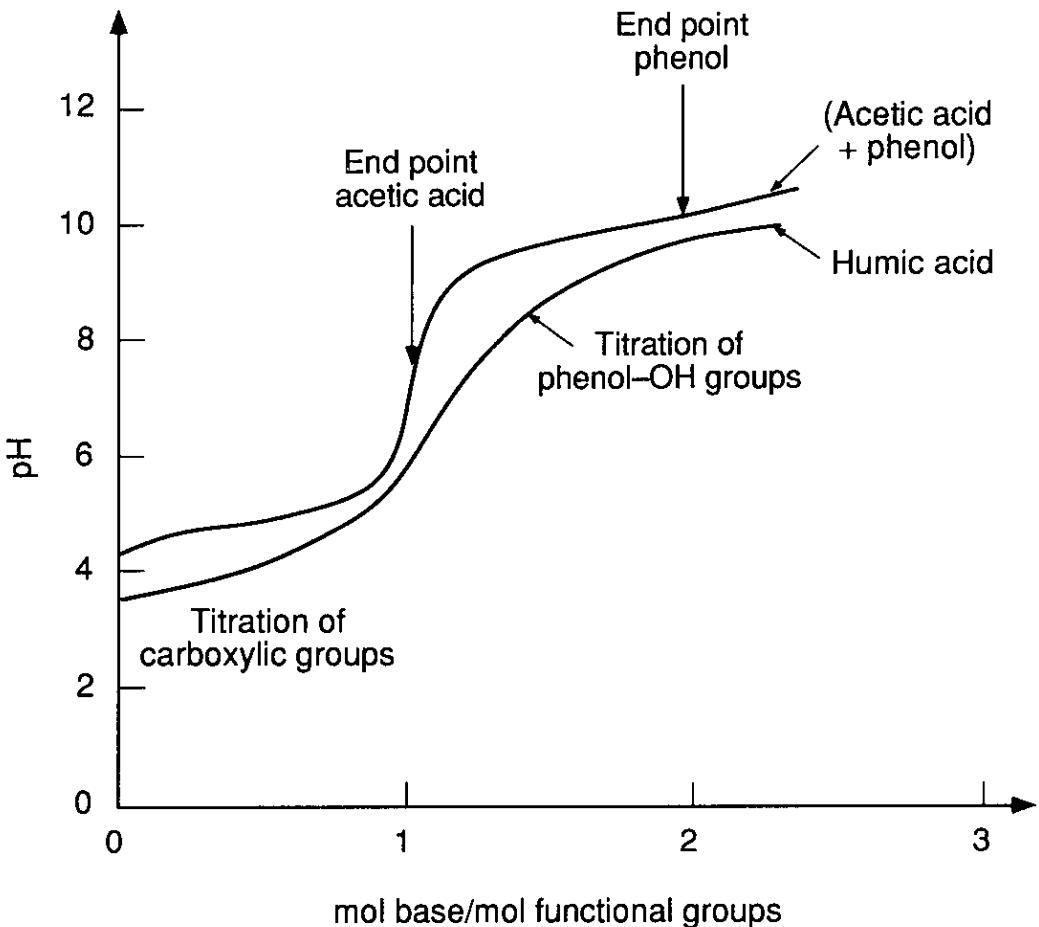
$$f = \frac{V_B N_B}{V_s M_s} = \frac{\text{equ}_B}{\text{moles}_s}$$

$$\text{pH}_i = 3.85 \quad \text{pK}_a = ??$$

$$\text{pK}_{as} = ??$$

Titration of Humics

- Model for aquatic humic substances
 - Acetic acid + phenol



Protons & Metals Ions

- Why??

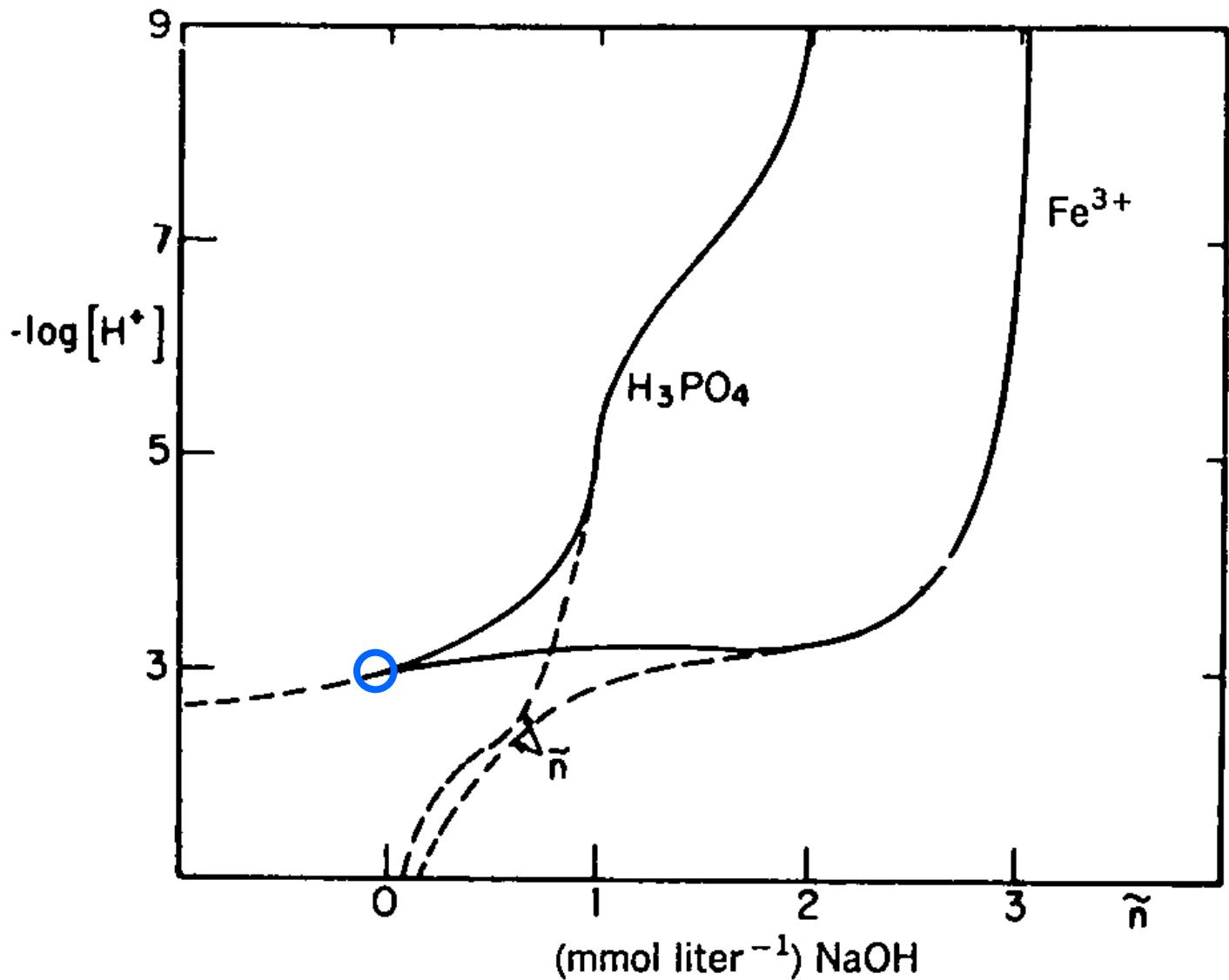
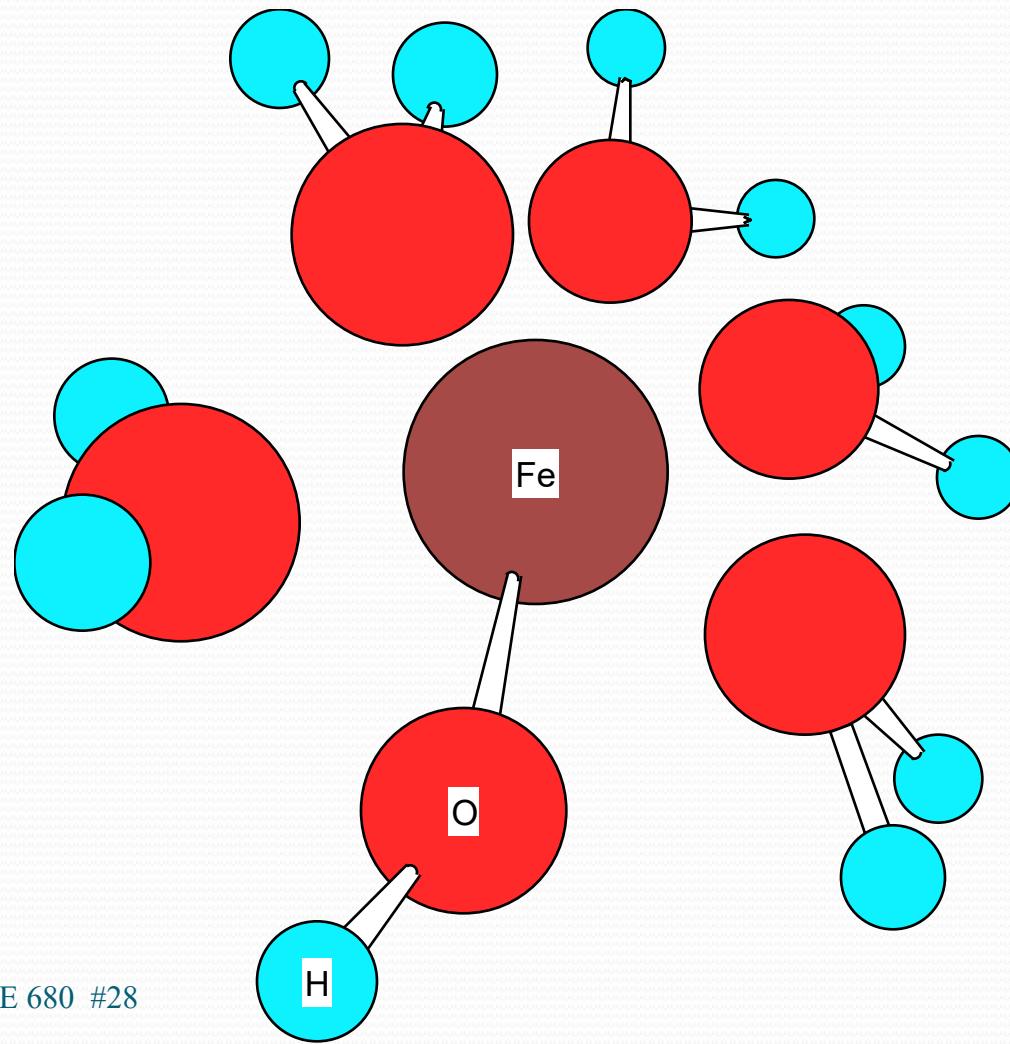
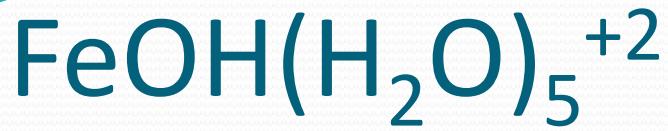
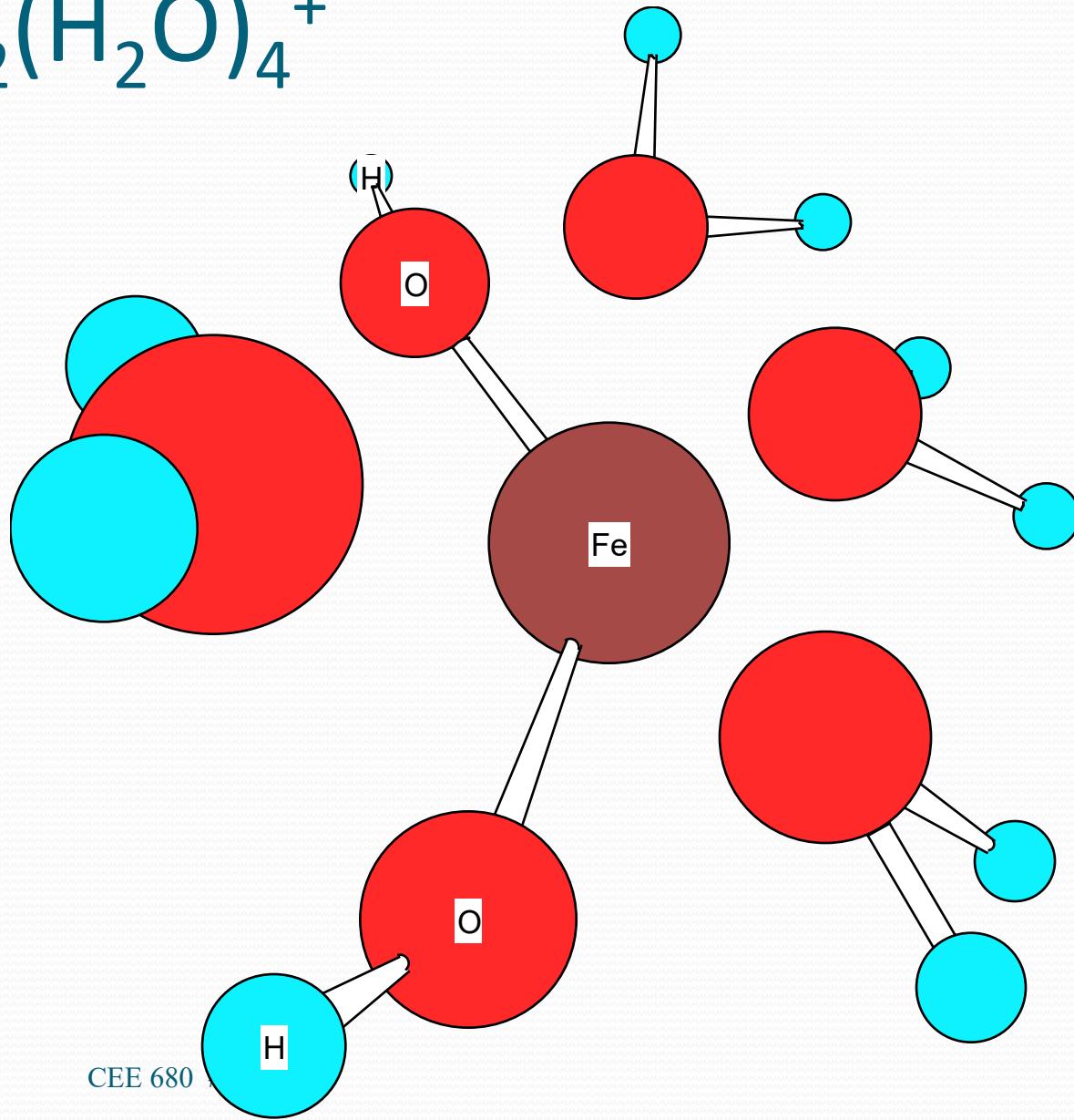
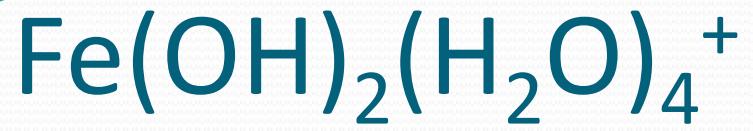
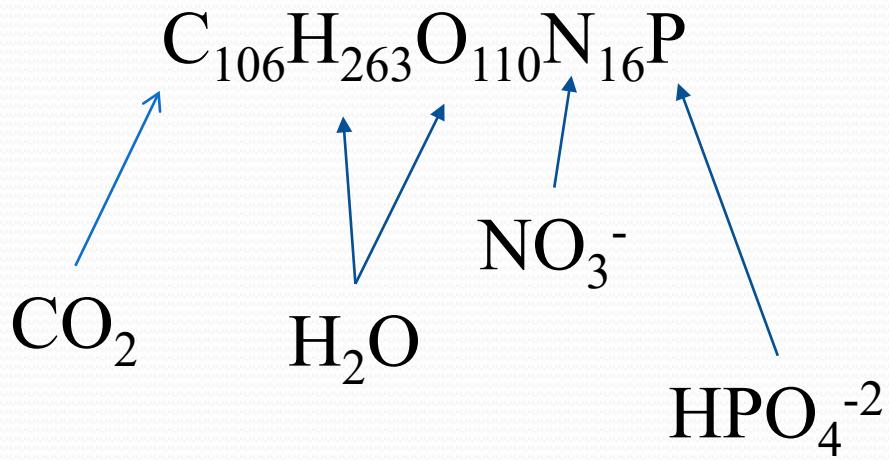
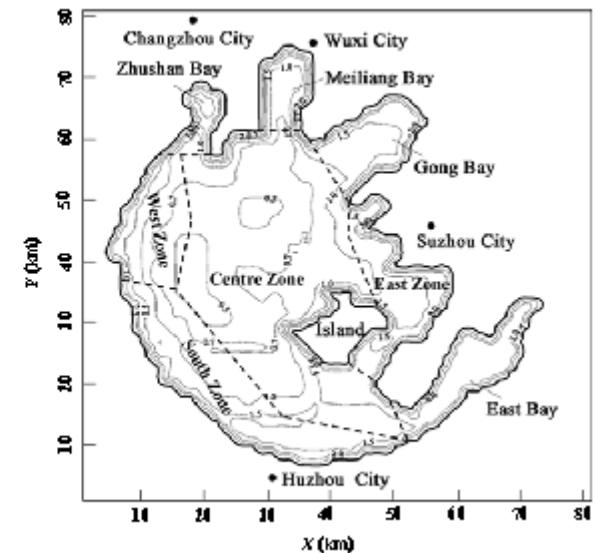


Fig 6.2
pg.259





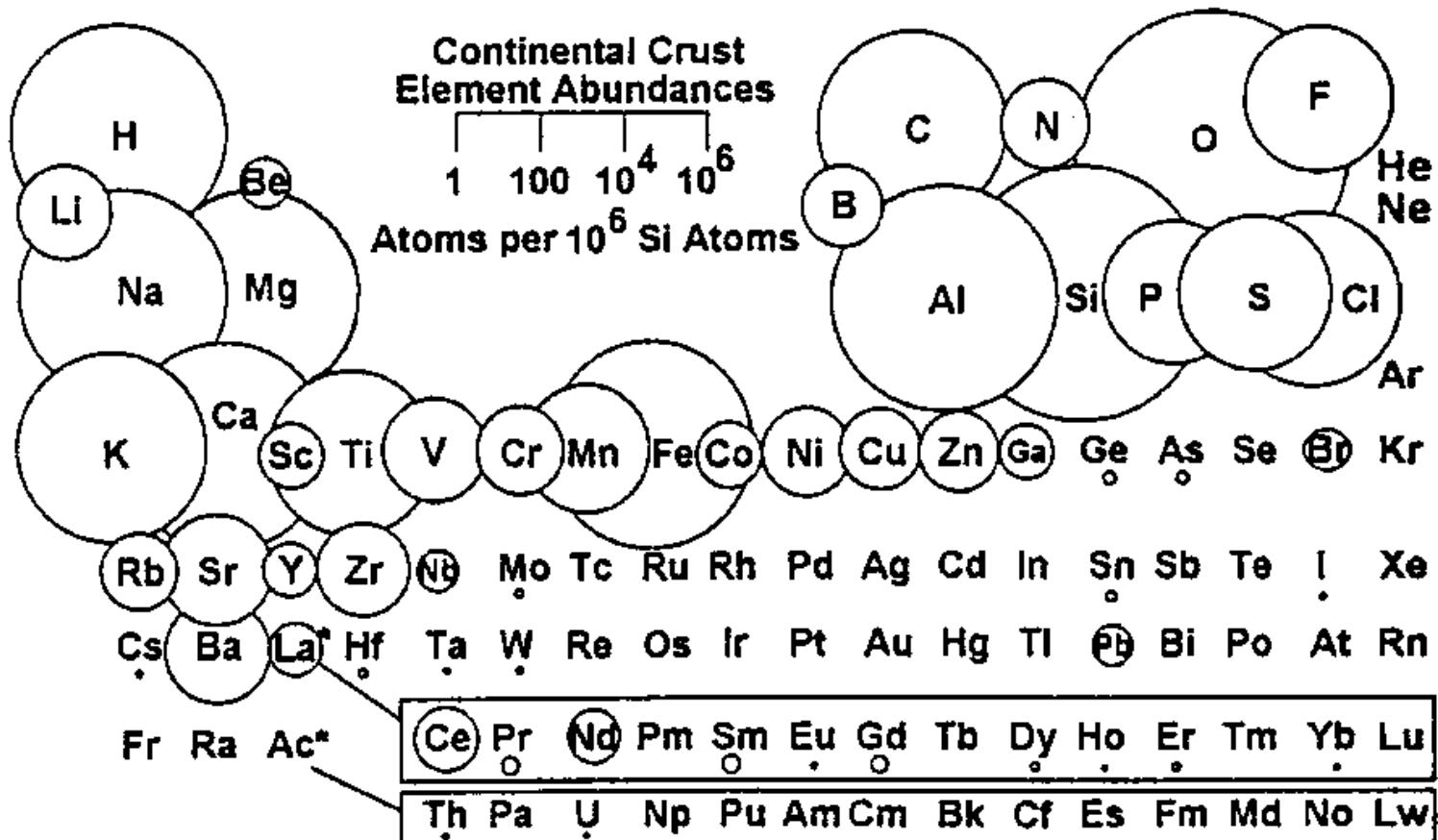
Limits to Growth



Another Problem Statement

- Photosynthesis with nitrate assimilation
 - $106 \text{ CO}_2 + 16 \text{ NO}_3^- + \text{HPO}_4^{2-} + 122 \text{ H}_2\text{O} + 18 \text{ H}^+$
= $\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 138 \text{ O}_2$
- Basis for stoichiometry and limits to growth
 - Algal cells are: $\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P}$
 - But what if they are: $\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P}_1\text{Fe}_{0.001}$

Elemental abundance in crust



- O
- Si
- Al
- Fe
- Ca
- Na
- Mg
- K
- Ti
- H
- P
- Mn
- F

Elemental abundance in fresh water

From: Stumm & Morgan, 1996; Benjamin, 2002; fig 1.1

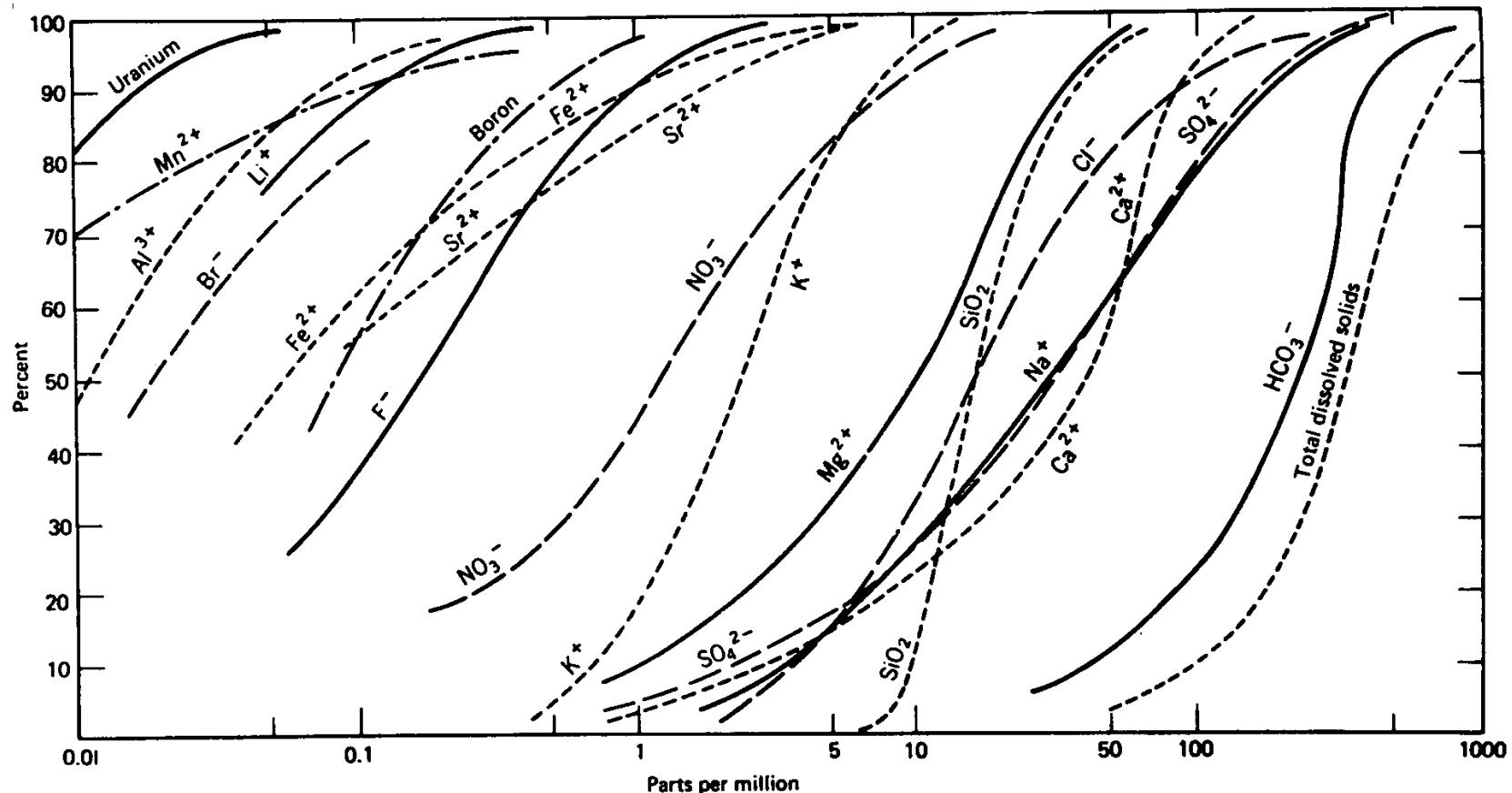


Figure 15.1. Cumulative curves showing the frequency distribution of various constituents in terrestrial water. Data are mostly from the United States from various sources. (Adapted from Davies and DeWiest, 1966.)

Complexation of hydroxide?

No

Yes, a bit

Periodic Table of the Elements																		
1 IA 11A	H Hydrogen 1.008	2 IIA 2A	3 Li Lithium 6.941	4 Be Beryllium 9.012	5 Vb 5B	6 Vib 6B	7 VIIb 7B	8	9 VIII 8	10 IB 1B	11 IIB 2B	12 Al Aluminum 26.982	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	
1 H Hydrogen 1.008	2 Be Beryllium 9.012	3 Li Lithium 6.941	4 Be Beryllium 9.012	5 Vb 5B	6 Vib 6B	7 VIIb 7B	8	9 VIII 8	10 IB 1B	11 IIB 2B	12 Al Aluminum 26.982	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIA 8A	
10 Ne Neon 20.180	11 Na Sodium 22.990	12 Mg Magnesium 24.305	13 Sc Scandium 44.956	14 Ti Titanium 47.88	15 V Vanadium 50.942	16 Cr Chromium 51.996	17 Mn Manganese 54.938	18 Fe Iron 55.933	19 Co Cobalt 58.933	20 Ni Nickel 58.693	21 Cu Copper 63.546	22 Zn Zinc 65.39	23 Ga Gallium 69.732	24 Ge Germanium 72.61	25 As Arsenic 74.922	26 Se Selenium 78.09	27 Br Bromine 79.904	28 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 Hf Hafnium 178.49	72 Ta Tantalum 180.948	73 W Tungsten 183.85	74 Re Rhenium 186.207	75 Os Osmium 190.23	76 Ir Iridium 192.22	77 Pt Platinum 195.08	78 Au Gold 196.967	79 Hg Mercury 200.59	80 Tl Thallium 204.383	81 Pb Lead 207.2	82 Bi Bismuth 208.980	83 Po Polonium [208.982]	84 At Astatine 209.987	85 Rn Radon 222.018	86 Uuo Ununoctium unknown	
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103 Ac Actinium [227.028]	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]		

Precipitation and Dissolution

- Environmental Significance
 - Engineered systems
 - coagulation, softening, removal of heavy metals
 - Natural systems
 - composition of natural waters
 - formation and composition of aquatic sediments
 - global cycling of elements
- Composition of natural waters
 - S&M, 3rd ed., figure 15.1 (pg. 873)

Intro: Chemical Reactions

- Driving force
 - Reactants strive to improve the stability of their electron configurations (i.e., lower ΔG)
- Types
 - **Redox reactions:** change in oxidation state
 - **Coordinative reactions:** change in coordinative relationships



Intro: Coordinative Reactions

- Definition: where the coordination number or coordination partner changes
- Types
 - Acid/base reactions



- Precipitation reactions



- Complexation reactions

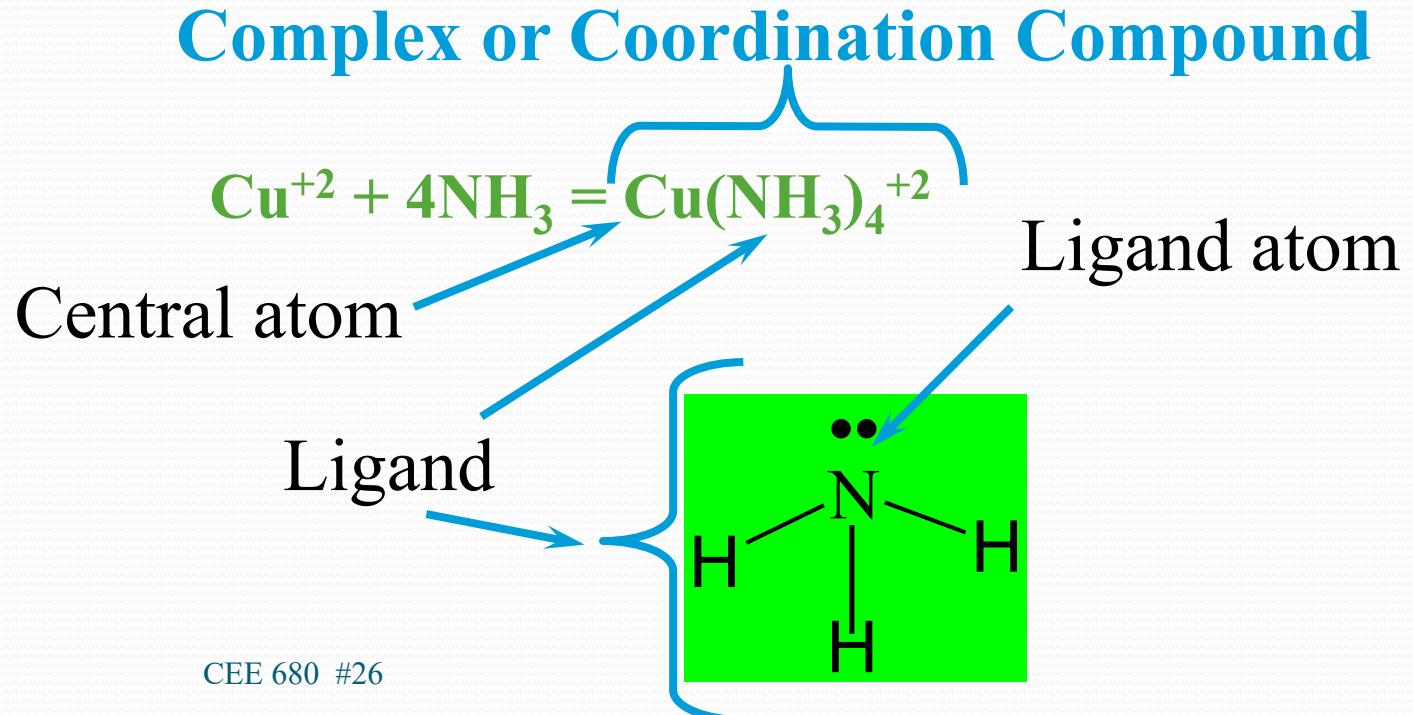


Coordination Chemistry: References

- Benjamin, 2002: Chapt. 8
 - Appendix A4
- Stumm & Morgan, 1996: Chapt. 6
- Butler, 1998: Chapt. 7 & 8
- Pankow, 1991: Chapt. 18
- Langmuir, 1997: Chapt. 3
- Snoeyink & Jenkins, 1980: Chapt. 5
- Morel & Hering, 1993: Chapt. 6
 - Morel, 1983: Chapt. 6
- Buffle, 1988: Chapt. 5 & 6

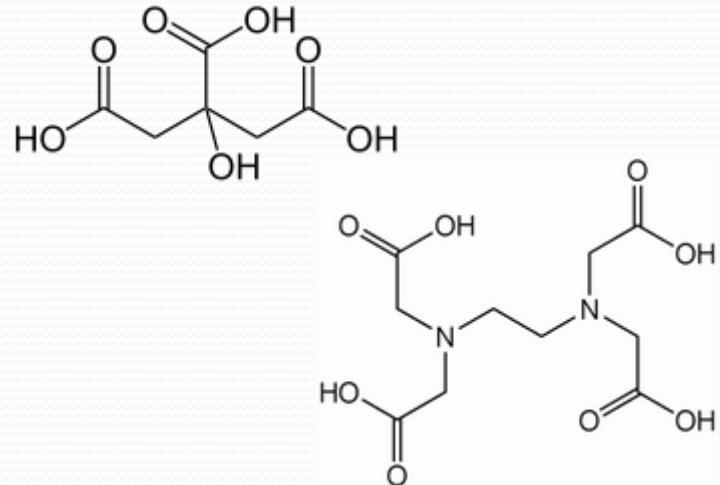
Coordination

- Definition
 - Any combining of cations with molecules or anions containing free pairs of electrons



Ligand types

- Constituent Ligand atoms
 - Nitrogen
 - Oxygen
 - Others: halides
- Numbers of active ligand atoms per ligand
 - One: monodentate (e.g., ammonia)
 - Two: bidentate (e.g., oxalate)
 - Three: tridentate (e.g., citrate)
 - Six: hexadentate (e.g., EDTA)



Multidentate
Resulting complexes
are called **chelates**

Coordination Basics

- Importance
 - Affects solubility of metals
 - e.g., Al(OH)_3 solubility
 - Used in Analytical chemistry
 - Determination of hardness
 - Metals act as buffers in natural waters
- Coordination Number
 - 1 for Hydrogen
 - 2, 4, or 6 for most metals

Ion Pairs & Complexes

- Two types of complex species
 - Ion Pairs
 - Ions of opposite charge that form an association of lesser charge
 - Ion pairs are separated by at least one water molecule
 - These are called “outer-sphere” complexes
 - Complexes
 - Metal ion and neutral or anionic ligand
 - Direct bond formed with no water molecule between
 - These are called “inner-sphere” complexes

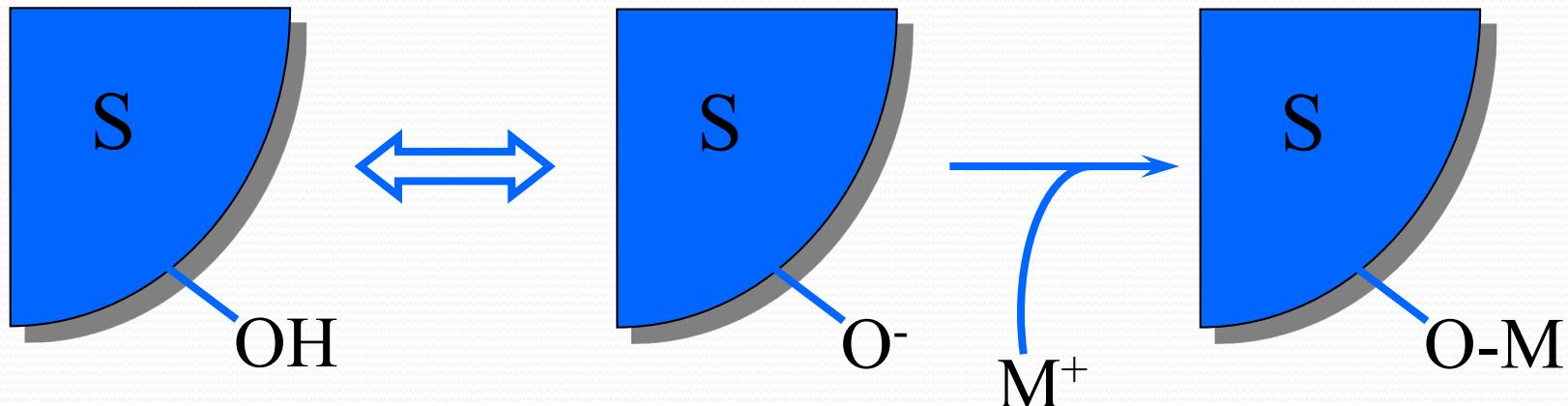
Ion pair stability

- Determined based on simple coulombic interactions

Ion Charge	Log K (I=0)	Log K (seawater)
1	0 to 1	-0.5 to 0.5
2	1.5 to 2.4	0.1 to 1.2
3	2.8 to 4.0	

Natural Particle as Ligands

- Natural Particles
 - High surface area
 - Usually coated with oxygen-containing surface groups which can donate electrons to metals (i.e., act as ligands)



Chemical Speciation

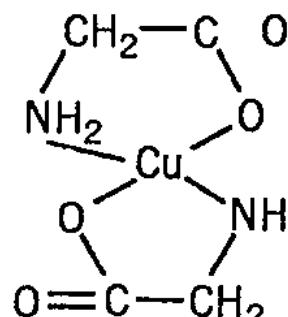
Free metal ion	Inorganic complexes	Organic complexes	Colloids Large polymers	Surface bound	Solid bulk phase, lattice
Cu-aq^{2+}	CuCO_3 CuOH^+ $\text{Cu}(\text{CO}_3)_2$ $\text{Cu}(\text{OH})_2$	 <p>Fulvate</p>	Inorganic Organic	$\text{Fe}-\overset{\text{O}}{\underset{\text{C}}{\text{O}}}-\text{Cu}$	CuO $\text{Cu}_2(\text{OH})_2\text{CO}_3$ Solid solution
True solution					
Dissolved		Particular			
Dialysis, gel filtration, membrane filtration					

Fig 6.1, pg. 258

Protons & Metals Ions

- All “free” metals and protons are actually hydrated in water
 - Both can bind with hydroxide

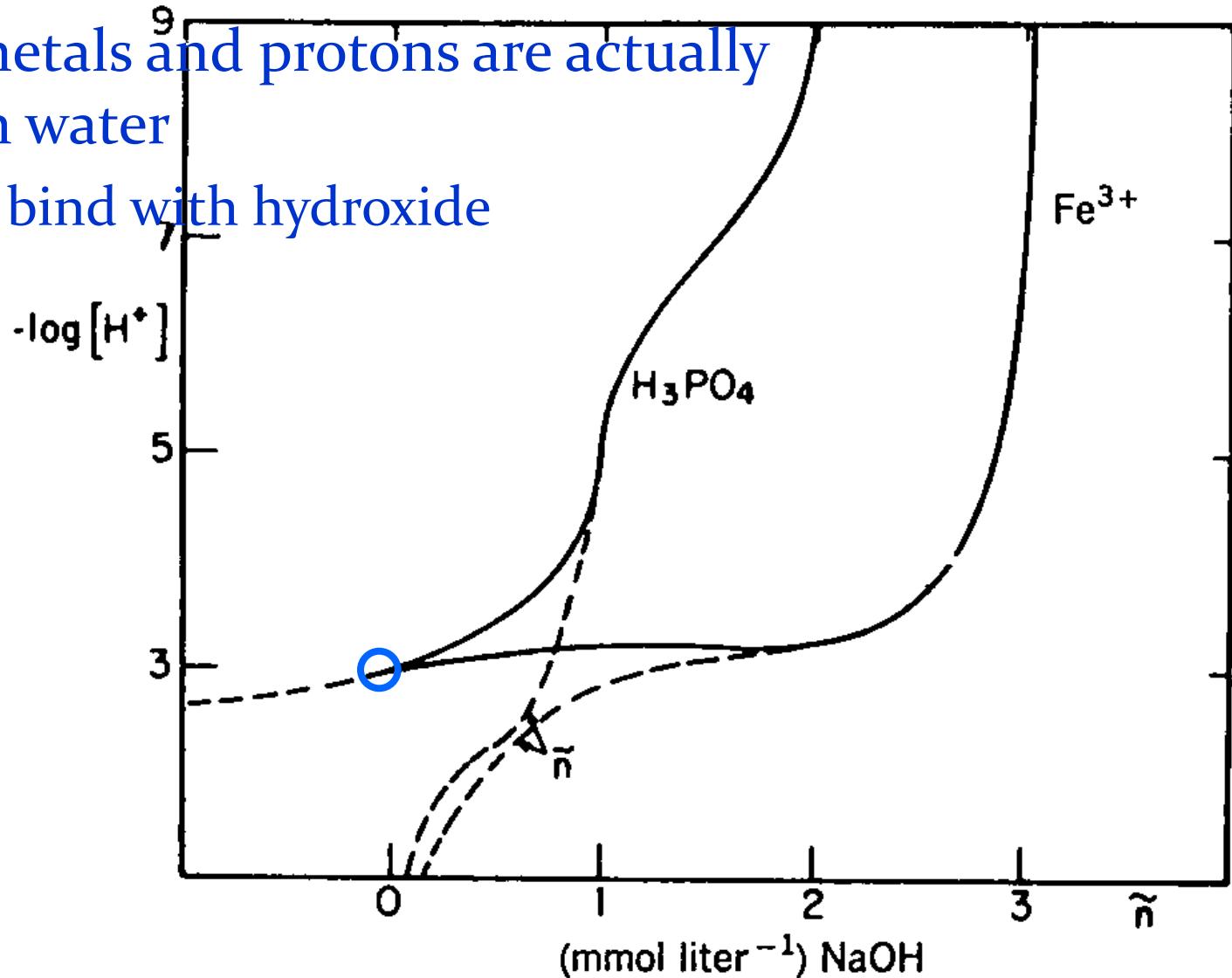


Fig 6.2
pg.259

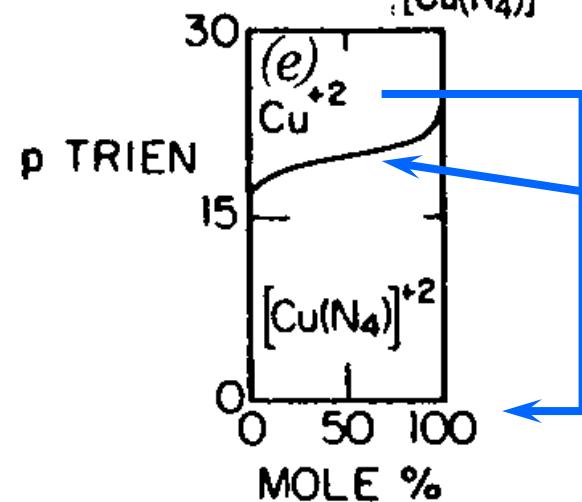
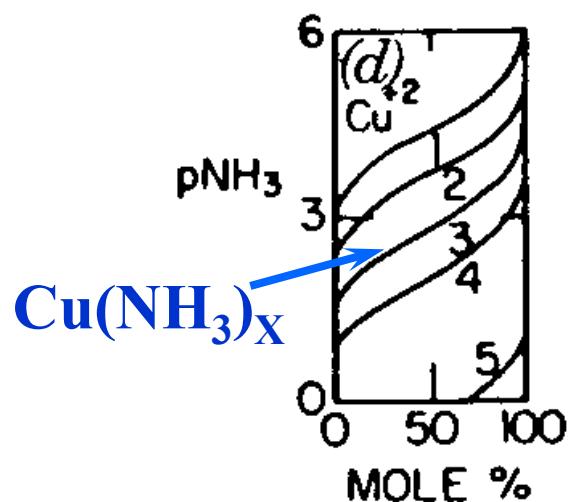
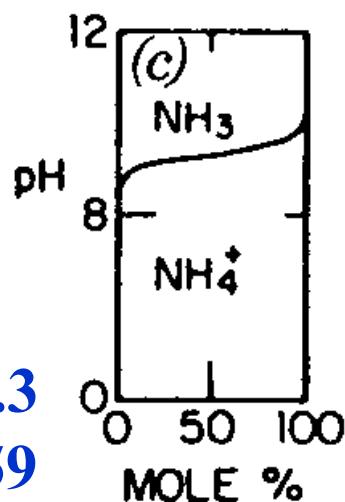
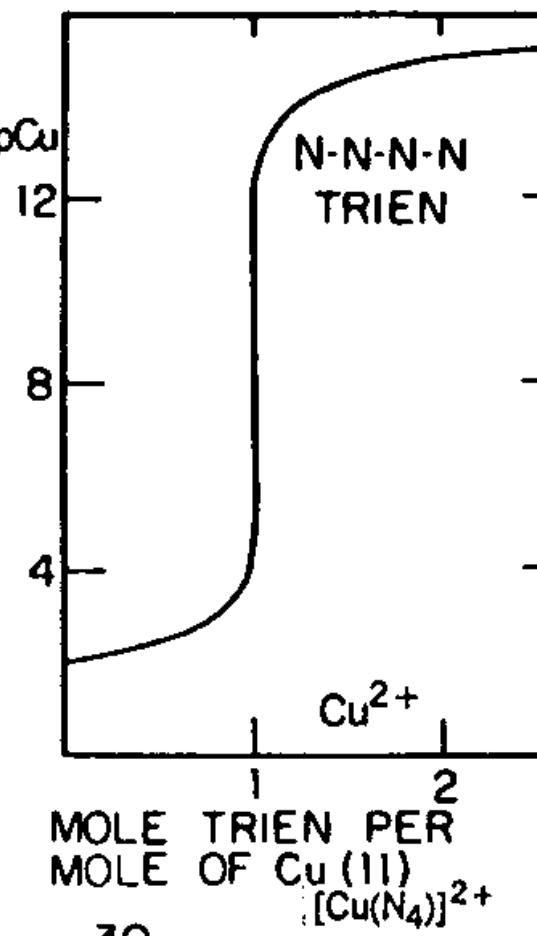
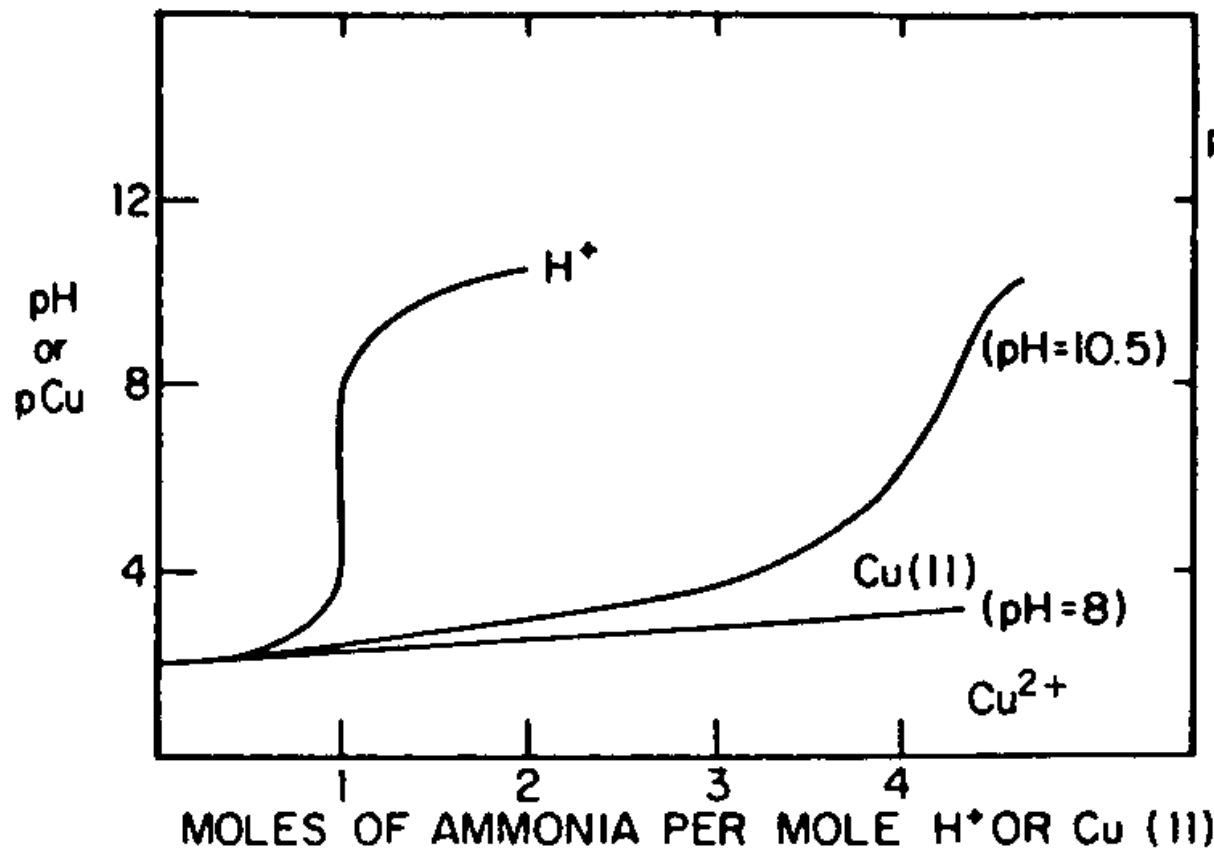


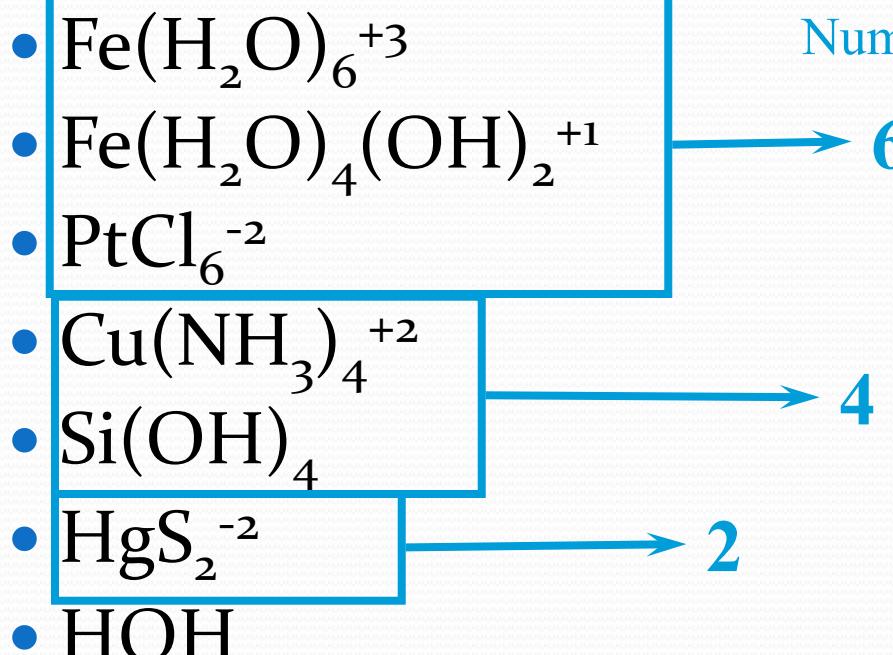
Fig 6.3
Pg.259

Brønsted & Lewis Acidity

- Definition of Acids
 - Brønsted: proton donors
 - Species with excess H⁺
 - Lewis: electron acceptors
 - H⁺, metal ions, others
- Strength
 - Tendency to accept electrons (or donate protons)
 - Measured by equilibrium constant

Complexes: Coordination

- $\text{Me}(\text{Ligand})_x$



Coordination
Number

6

4

2

Coordination # Depends on:

1. Size of central Atom
2. Charge of central Atom
3. Size of Ligand

- To next lecture