Updated: 4 March 2020

Print version

CEE 680: Water Chemistry

Lecture #26

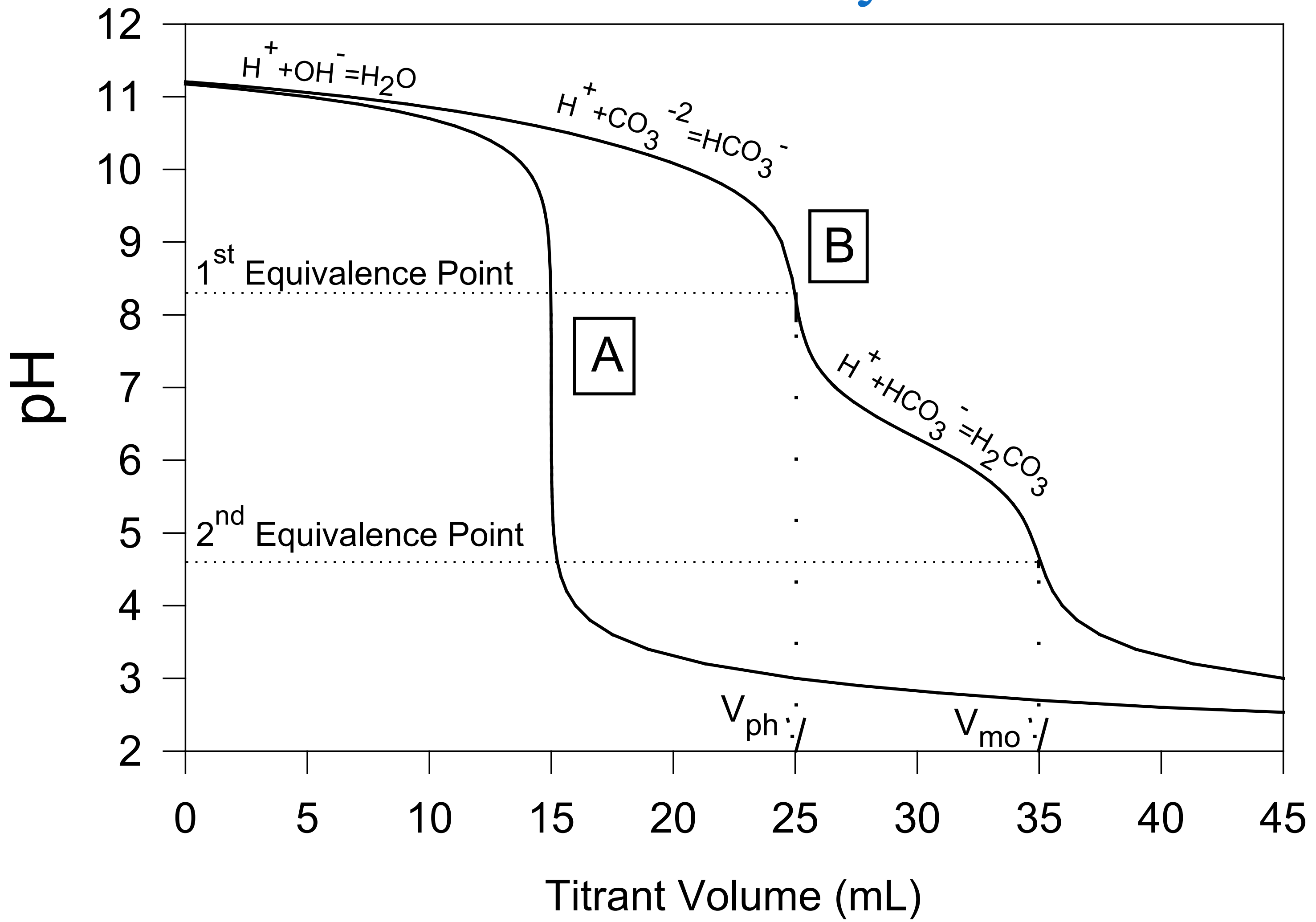
Coordination Chemistry: Hydrolysis

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

Benjamin; Chapter 8.1-8.6

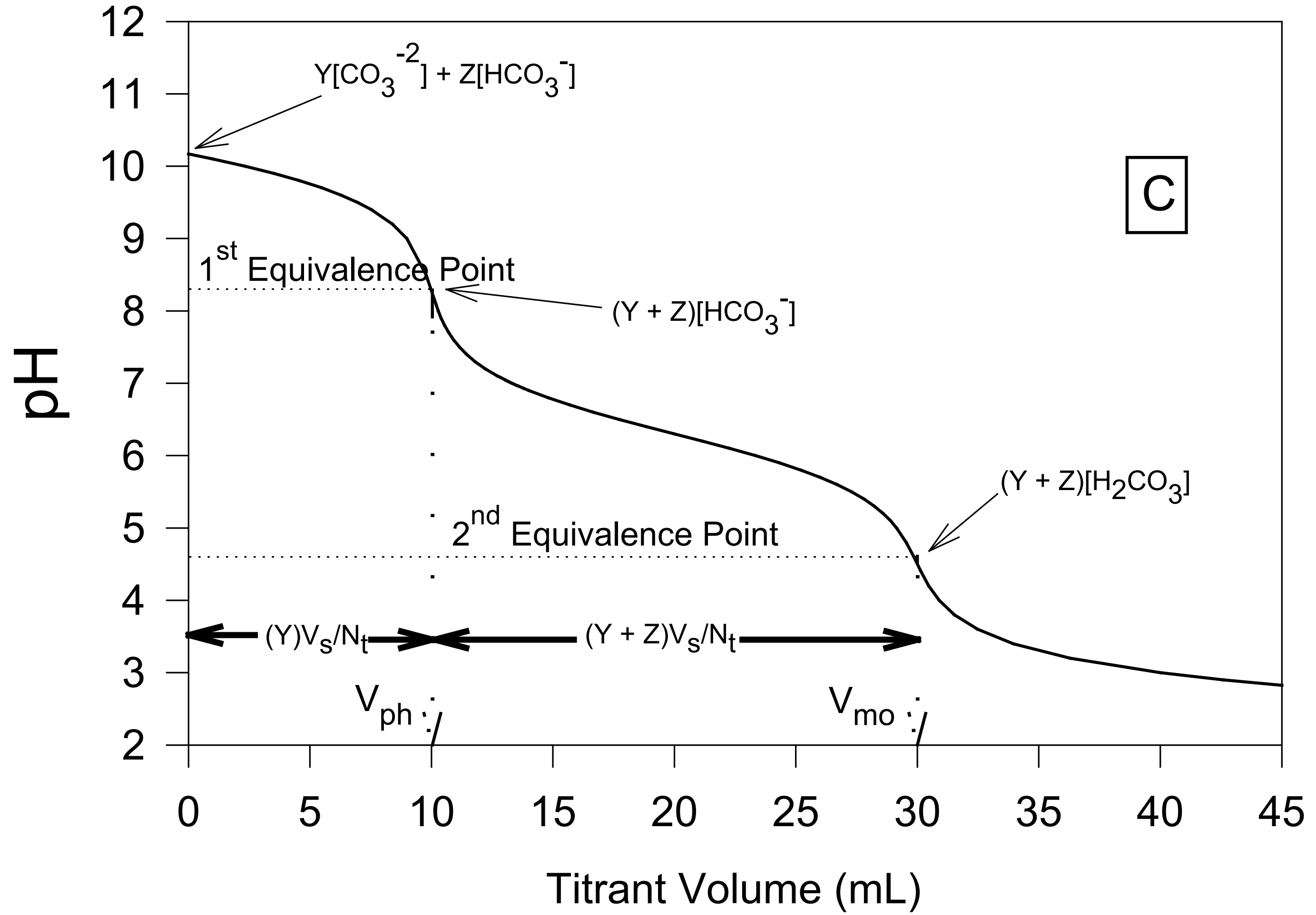
Acid Titration Curve for a Water Containing Hydroxide and Carbonate Alkalinity

From Lecture #20



Acid Titration Curve for a Water Containing Carbonate and Bicarbonate Alkalinity

From Lecture #20



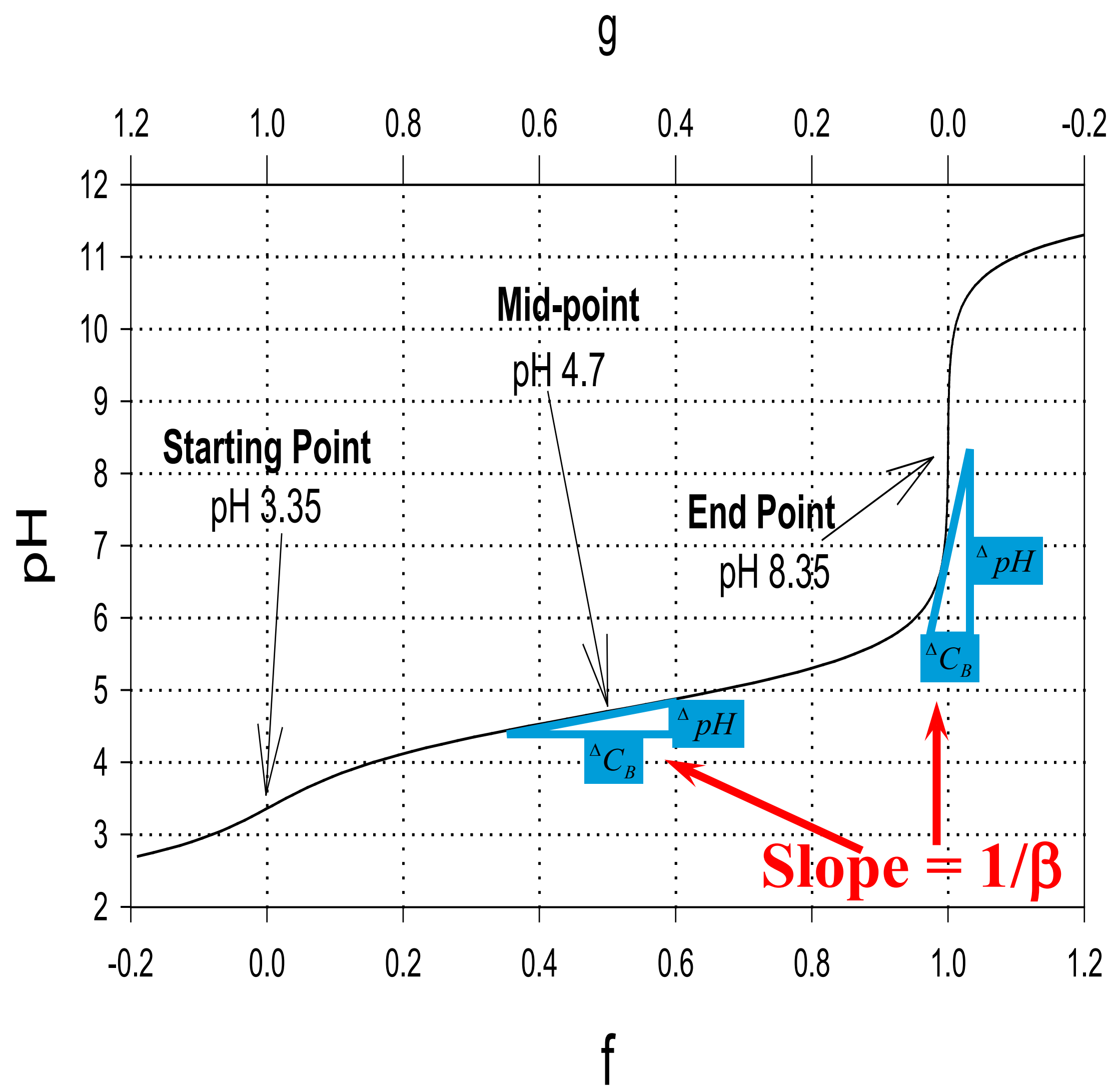
Buffer Intensity

10^{-2}M HAc

From Lecture #17

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

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



Base titration of an acid

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

$$f = \frac{V_B N_B}{V_s M_s} = \frac{equ_B}{moles_s} = \frac{C_B}{C_T}$$

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

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

$$\alpha_1 = \frac{1}{\frac{[H^+]}{K_a}+1}$$

- For a diprotic
  - Using the same ENE approach

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

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

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

$$\alpha_1 = \frac{1}{\frac{[H^+]}{K_1}+1+\frac{K_2}{[H^+]}}$$

Example Titration

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

$$f = \frac{V_B N_B}{V_s M_s} = \frac{equ_B}{moles_s}$$

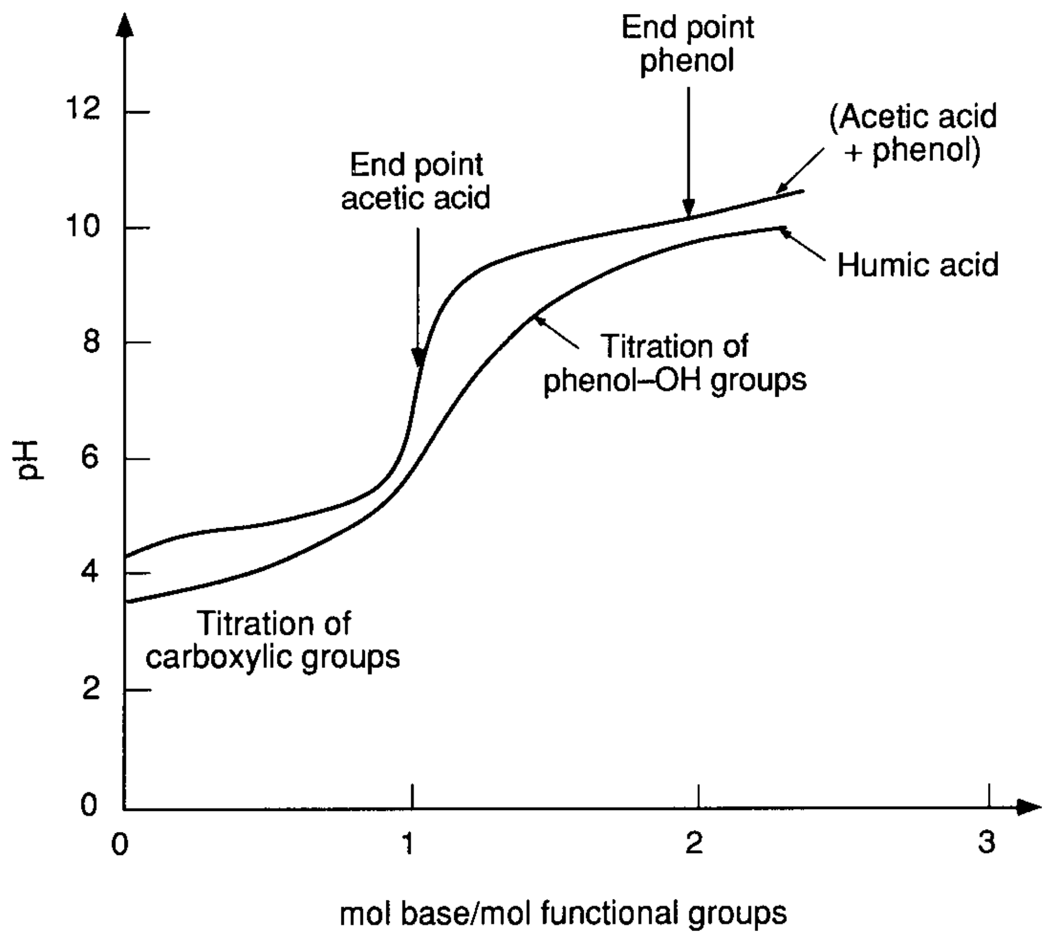
$pH_i = 3.85$ $pK_a = ??$

$pK_{as} = ??$

Titration of Humics

From Lecture #18

- Model for aquatic humic substances
  - Acetic acid + phenol



Protons & Metals Ions

- Why??

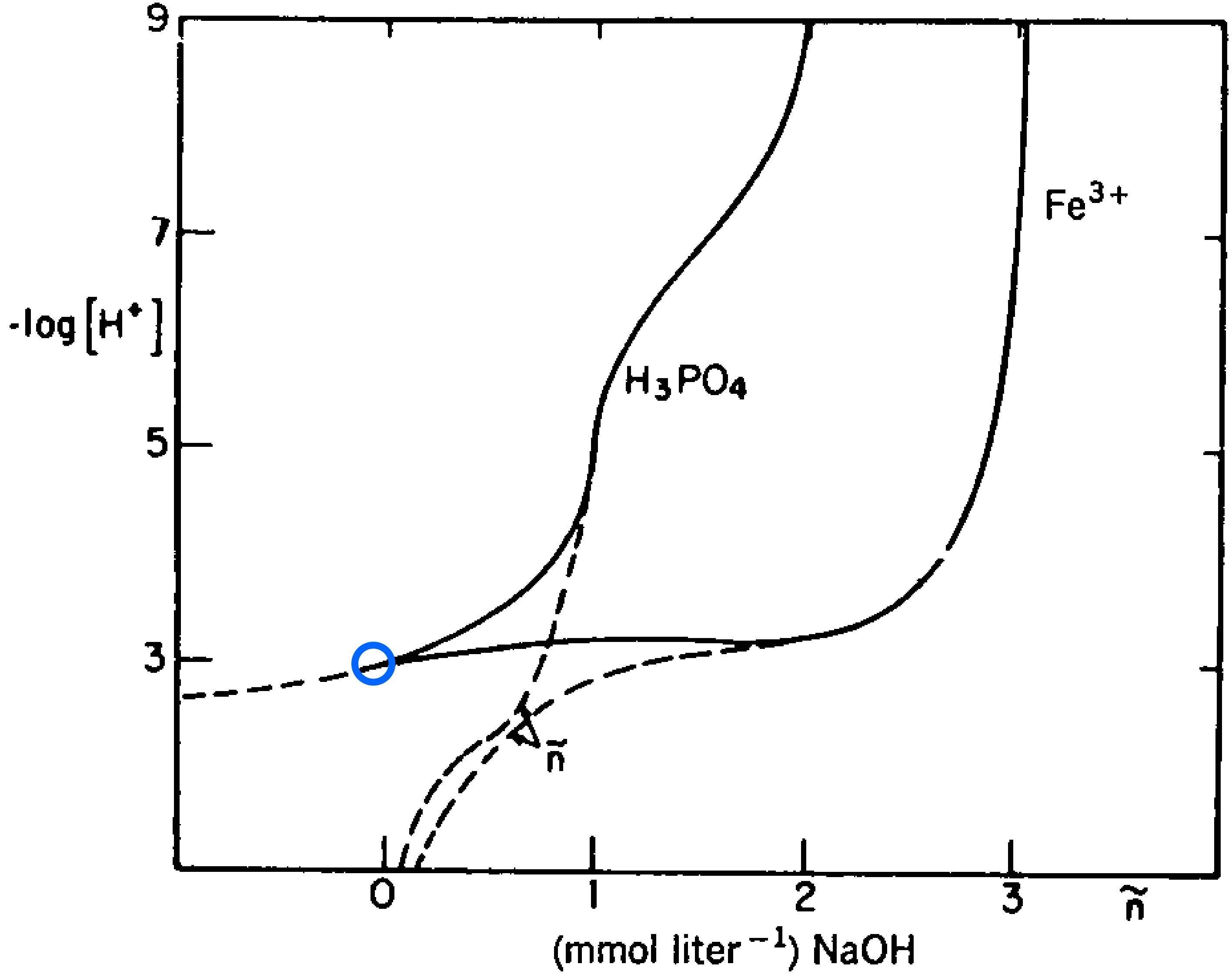
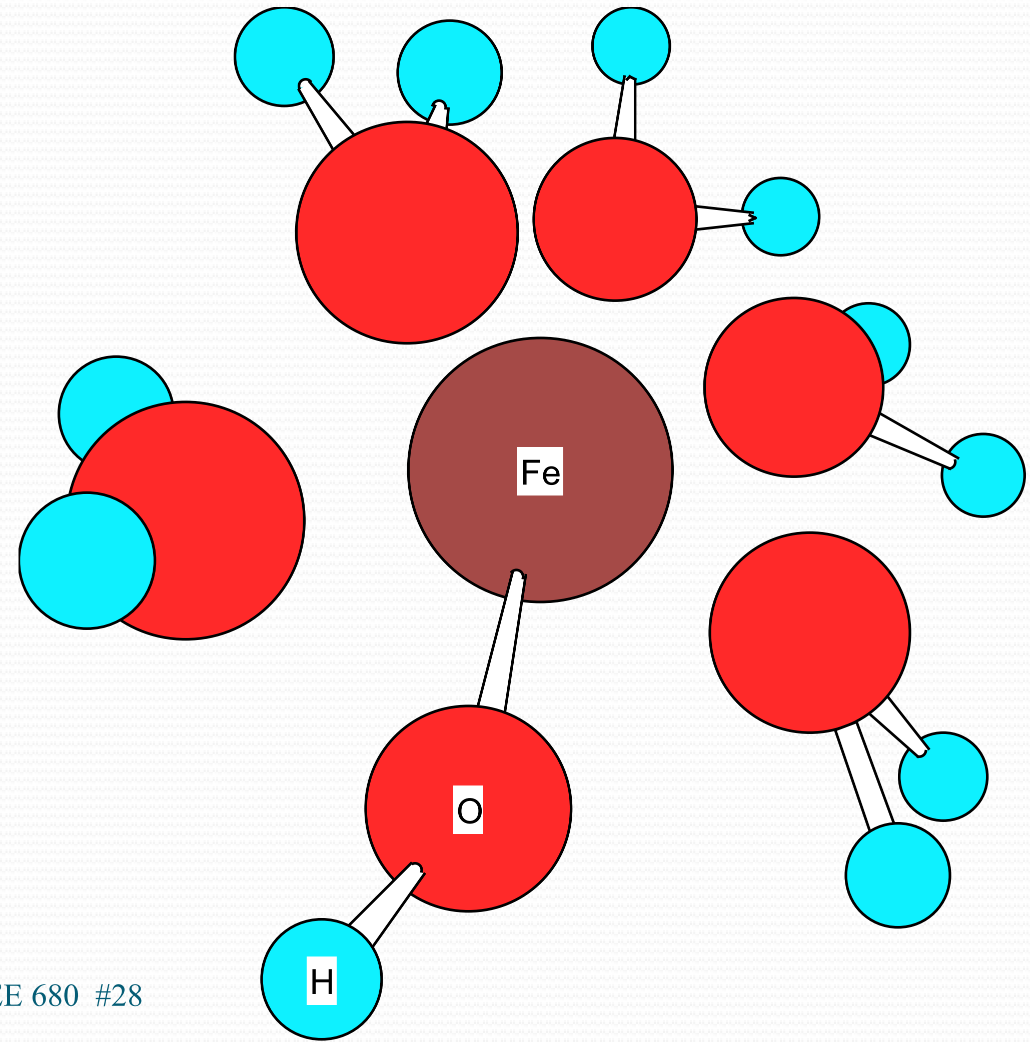
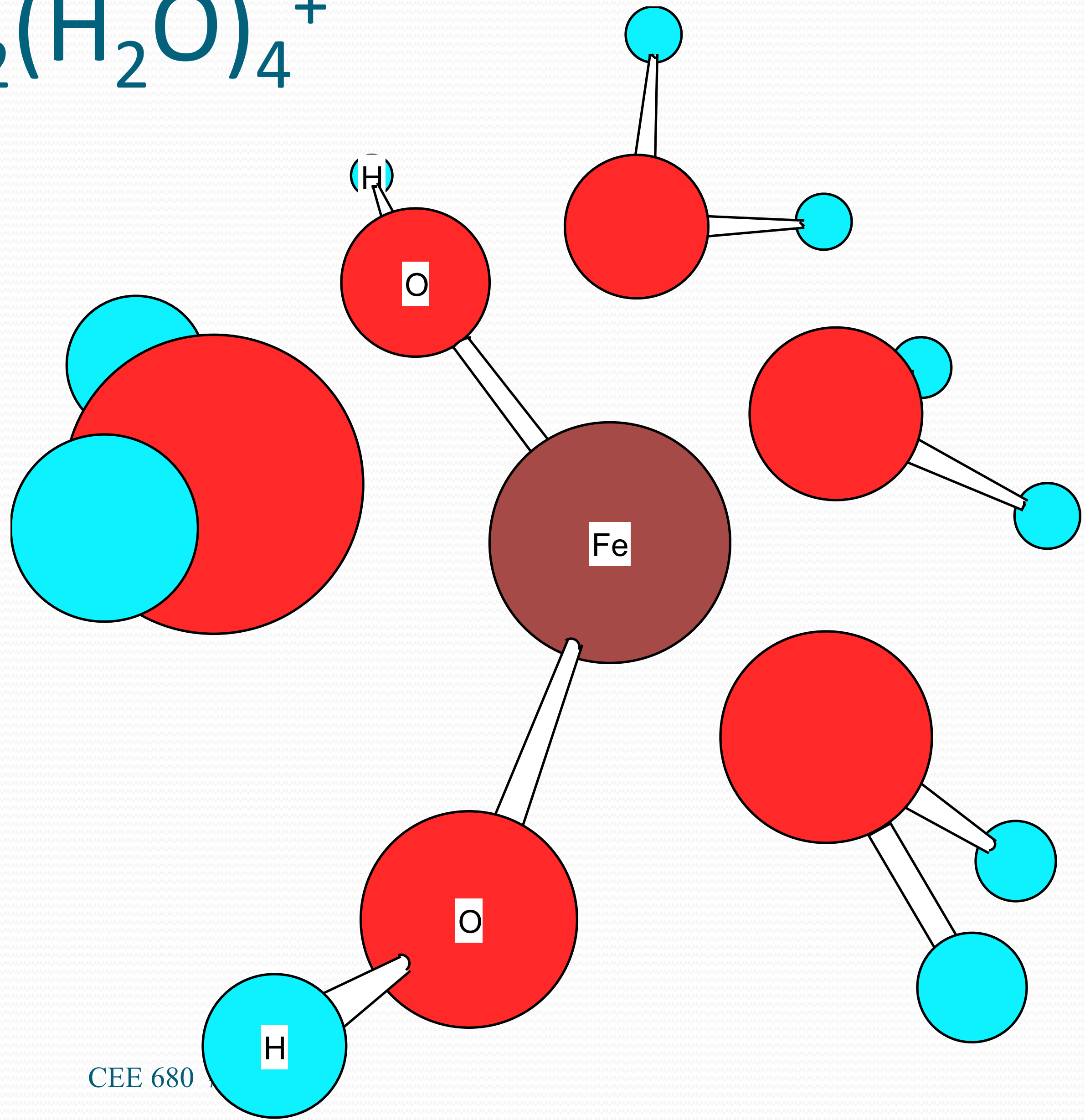


Fig 6.2
pg.259

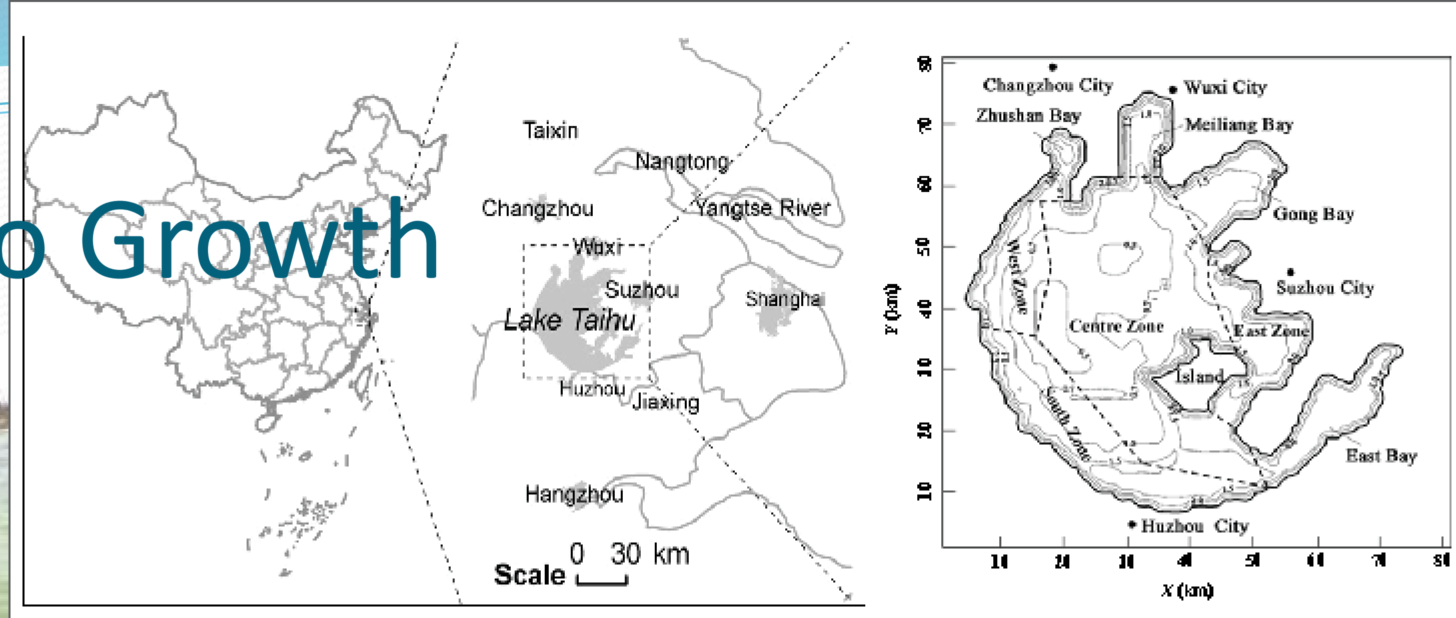
$FeOH(H_2O)_5^{+2}$



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



Limits to Growth



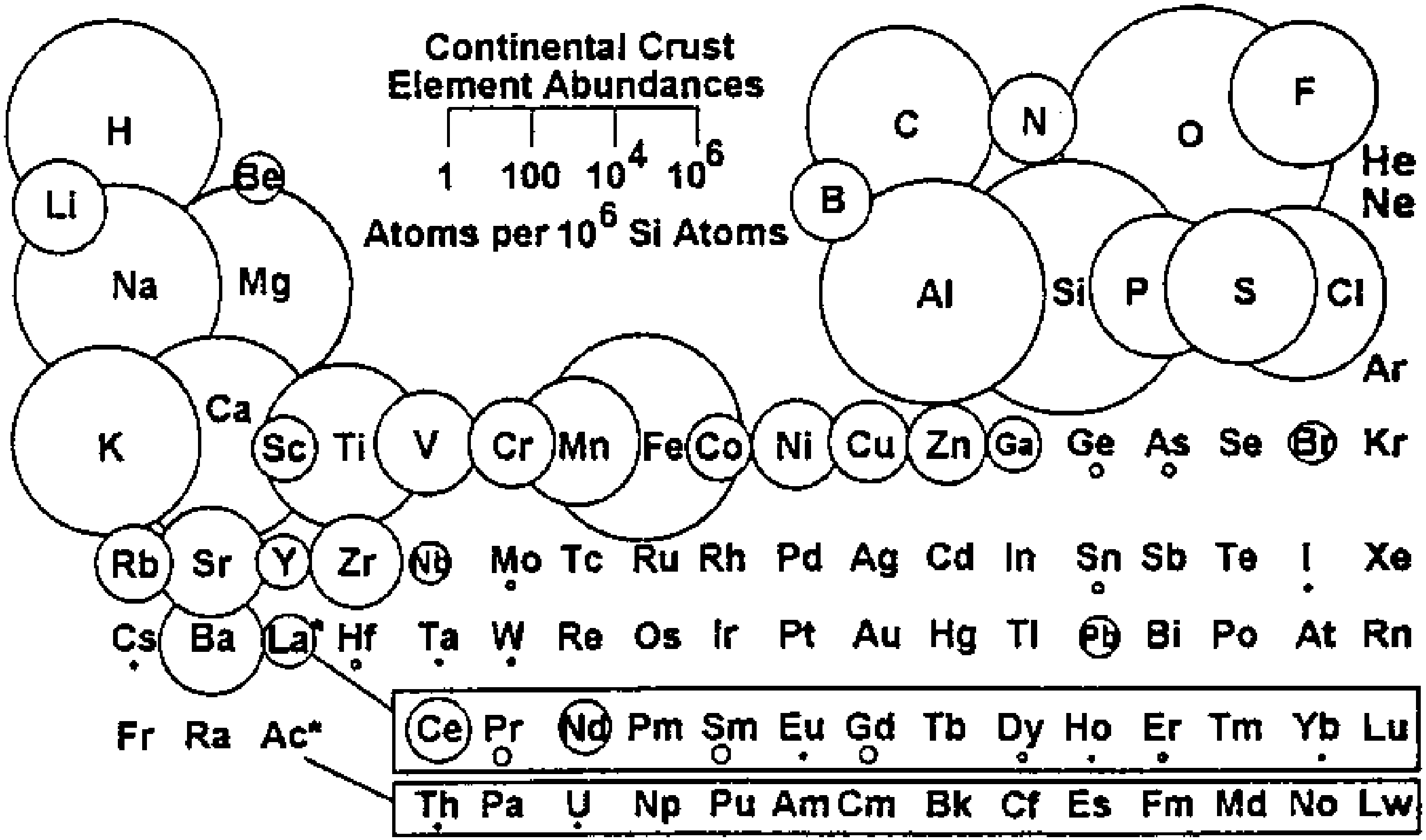
$$C_{106}H_{263}O_{110}N_{16}P$$

CO_2 H_2O NO_3^- HPO_4^{-2}

Another Problem Statement

- Photosynthesis with nitrate assimilation
  - $106\ CO_2 + 16\ NO_3^- + HPO_4^{-2} + 122\ H_2O + 18\ H^+$
    $= \quad C_{106}H_{263}O_{110}N_{16}P + 138\ O_2$
- Basis for stoichiometry and limits to growth
  - Algal cells are: $C_{106}H_{263}O_{110}N_{16}P$
  - But what if they are: $C_{106}H_{263}O_{110}N_{16}P_1Fe_{0.001}$

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

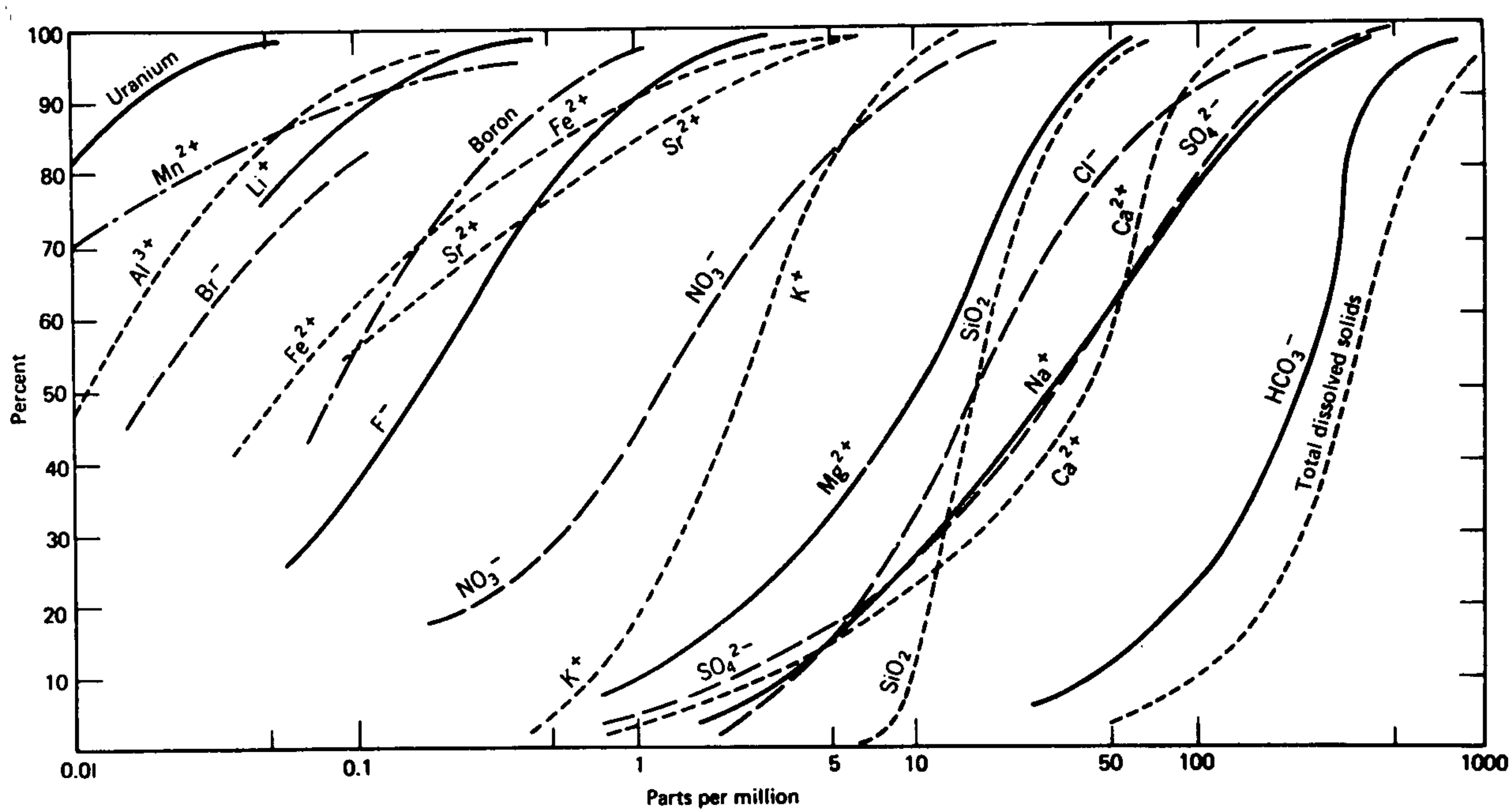
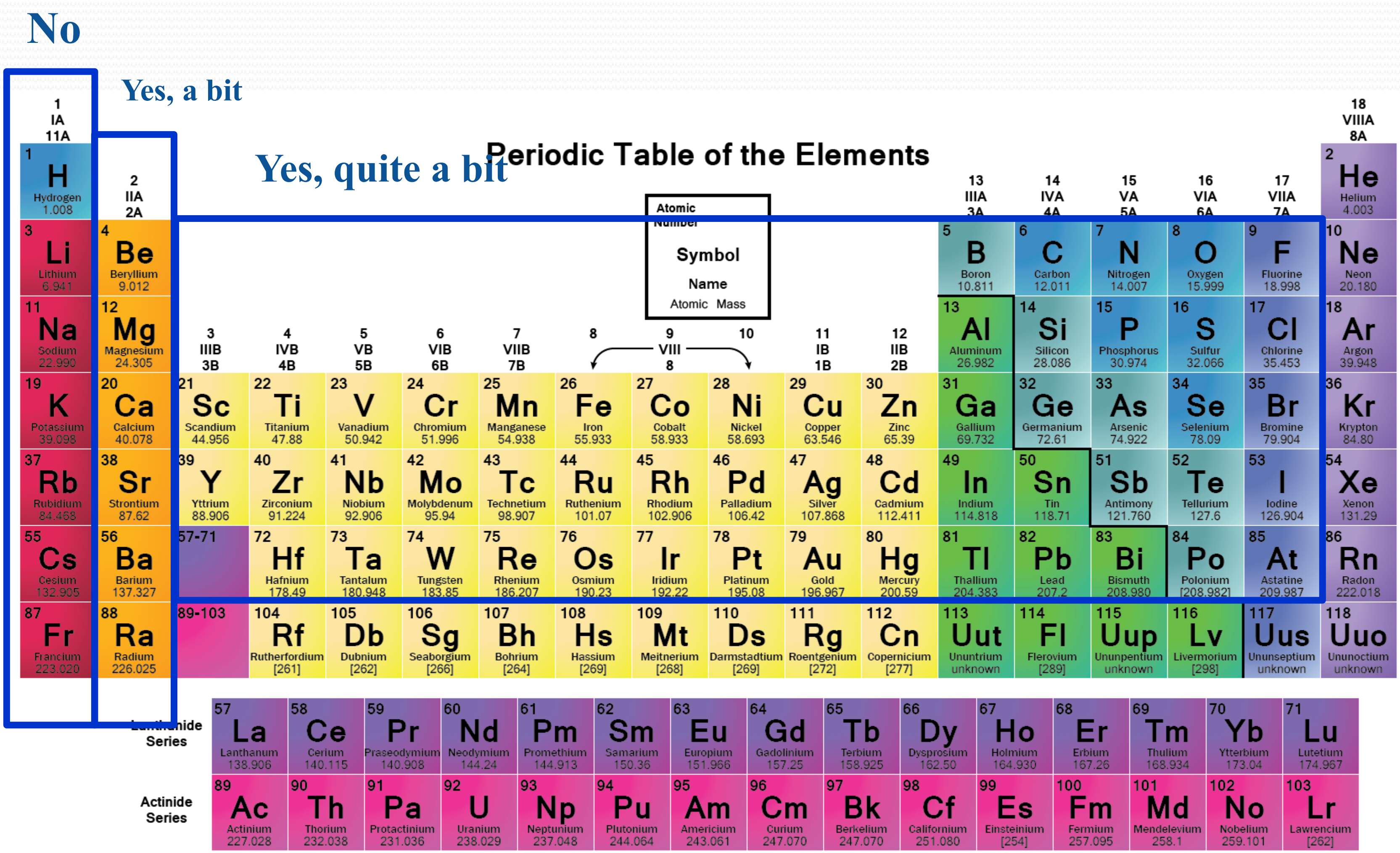


Figure 15.1. Cumulative curves showing the frequency distribution of various constituents in terrestrial water. Data are mostly from the United States from various sources. (Adapted from Davies and DeWiest, 1966.)

Complexation of hydroxide?



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

$$HClO = H^+ + ClO^-$$

$$HClO + H_2O = H_3O^+ + ClO^-$$

  - Precipitation reactions

$$Mg^{+2} + 2OH^- = Mg(OH)_{2(s)}$$

$$Mg(H_2O)_2^{+2} + 2OH^- = Mg(OH)_{2(s)} + 2H_2O$$

  - Complexation reactions

$$Cu^{+2} + 4NH_3 = Cu(NH_3)_4^{+2}$$

$$Cu(H_2O)_4^{+2} + 4NH_3 = Cu(NH_3)_4^{+2} + 4H_2O$$

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

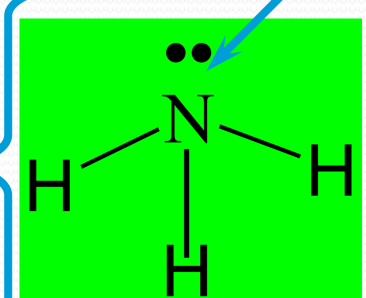
Complex or Coordination Compound

$$Cu^{+2} + 4NH_3 = \underbrace{Cu(NH_3)_4^{+2}}$$

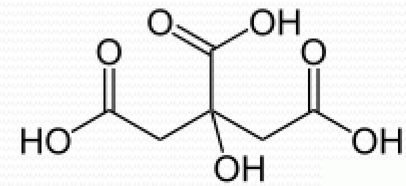
Central atom

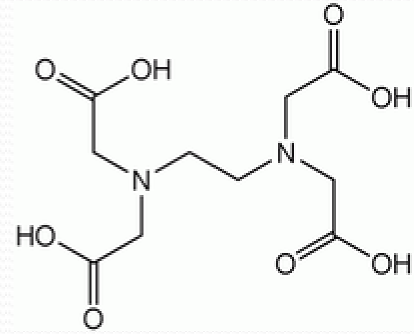
Ligand atom

Ligand



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

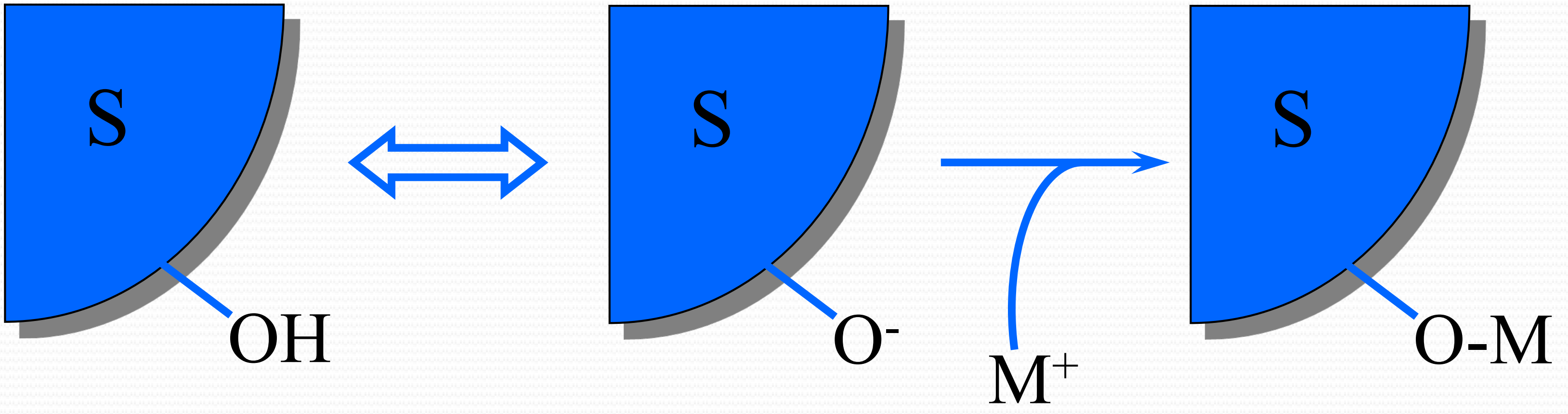
Ion pair stability

- Determined based on simple coulombic interactions

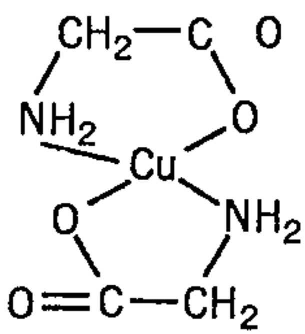
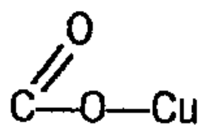
Ion Charge	Log K (I=0)	Log K (seawater)
1	0 to 1	-0.5 to 0.5
2	1.5 to 2.4	0.1 to 1.2
3	2.8 to 4.0	

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
$Cu{-}aq^{2+}$	$CuCO_3$ $CuOH^+$ $Cu(CO_3)_2$ $Cu(OH)_2$	 Fulvate	Inorganic Organic	Fe—OCu 	CuO $Cu_2(OH)_2CO_3$ 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

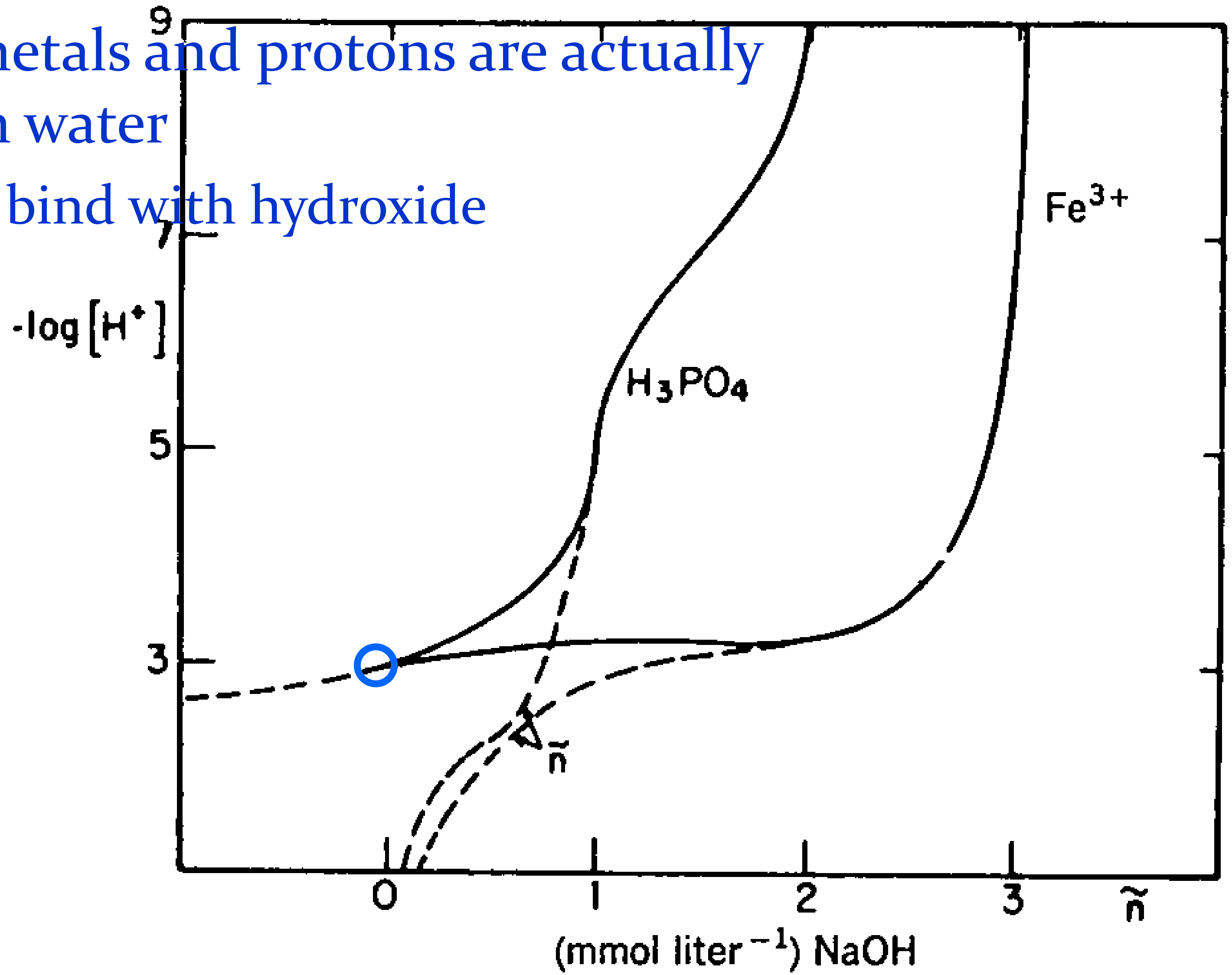
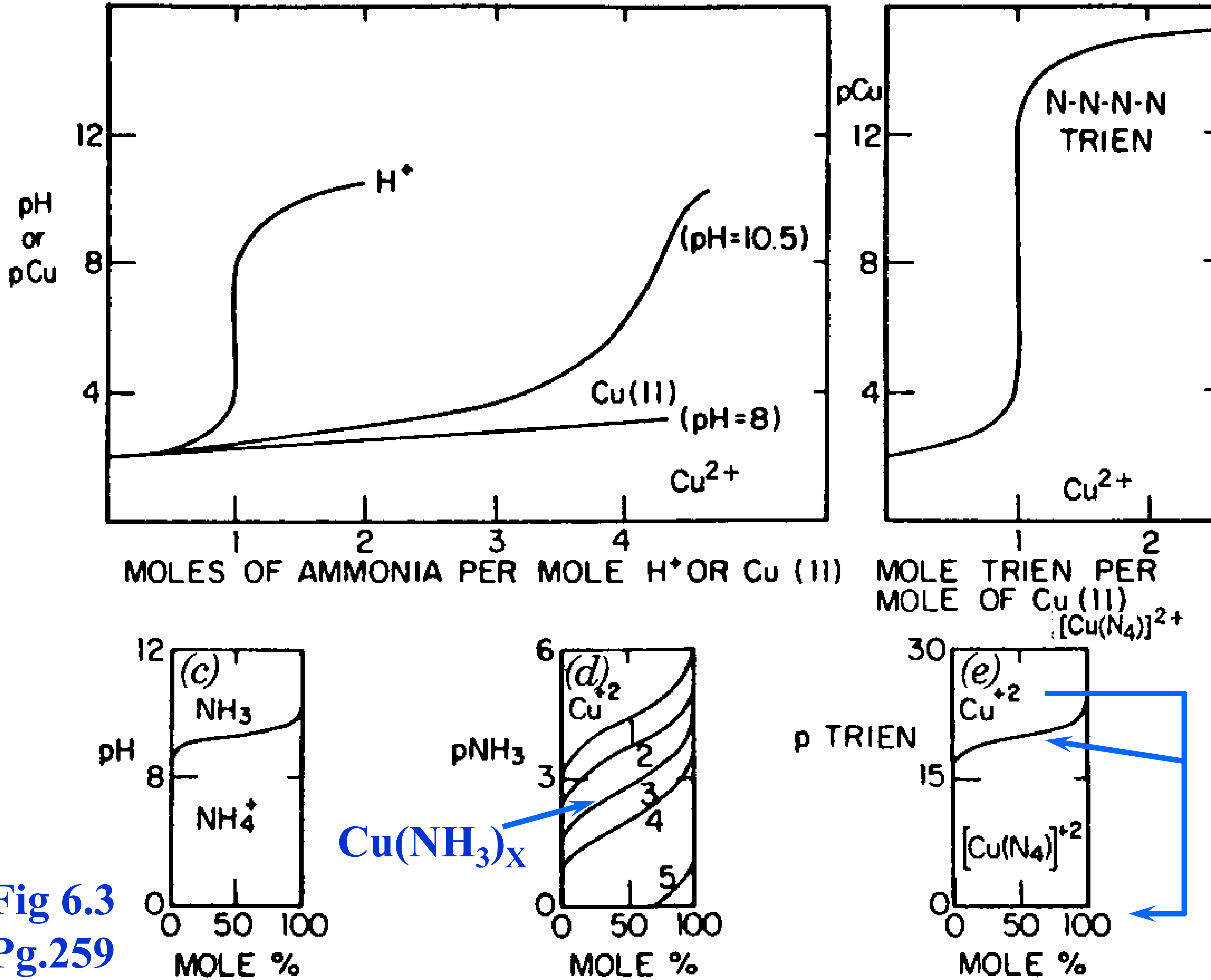


Fig 6.2
pg.259



pH
or
pCu
12
8
4
H+
(pH=10.5)
Cu(II)
(pH=8)
Cu2+
1
2
3
4
MOLES OF AMMONIA PER MOLE H+OR Cu (II)
pCu
N-N-N-N
TRIEN
MOLE TRIEN PER
MOLE OF Cu (II)
[Cu(N4)]2+
(c)
NH3
NH4+
pH
0
50
100
MOLE %
(d)
Cu+2
pNH3
6
3
2
3
4
5
Cu(NH3)X
(e)
Cu+2
p TRIEN
30
15
[Cu(N4)]+2

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

- $Me(Ligand)_x$
  - $Fe(H_2O)_6^{+3}$
  - $Fe(H_2O)_4(OH)_2^{+1}$
  - $PtCl_6^{-2}$
  - $Cu(NH_3)_4^{+2}$
  - $Si(OH)_4$
  - HgS_2^{-2}
  - HOH

Coordination Number

6

4

2

<u>Coordination # Depends on</u>:

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

- To next lecture