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CEE 680: Water Chemistry

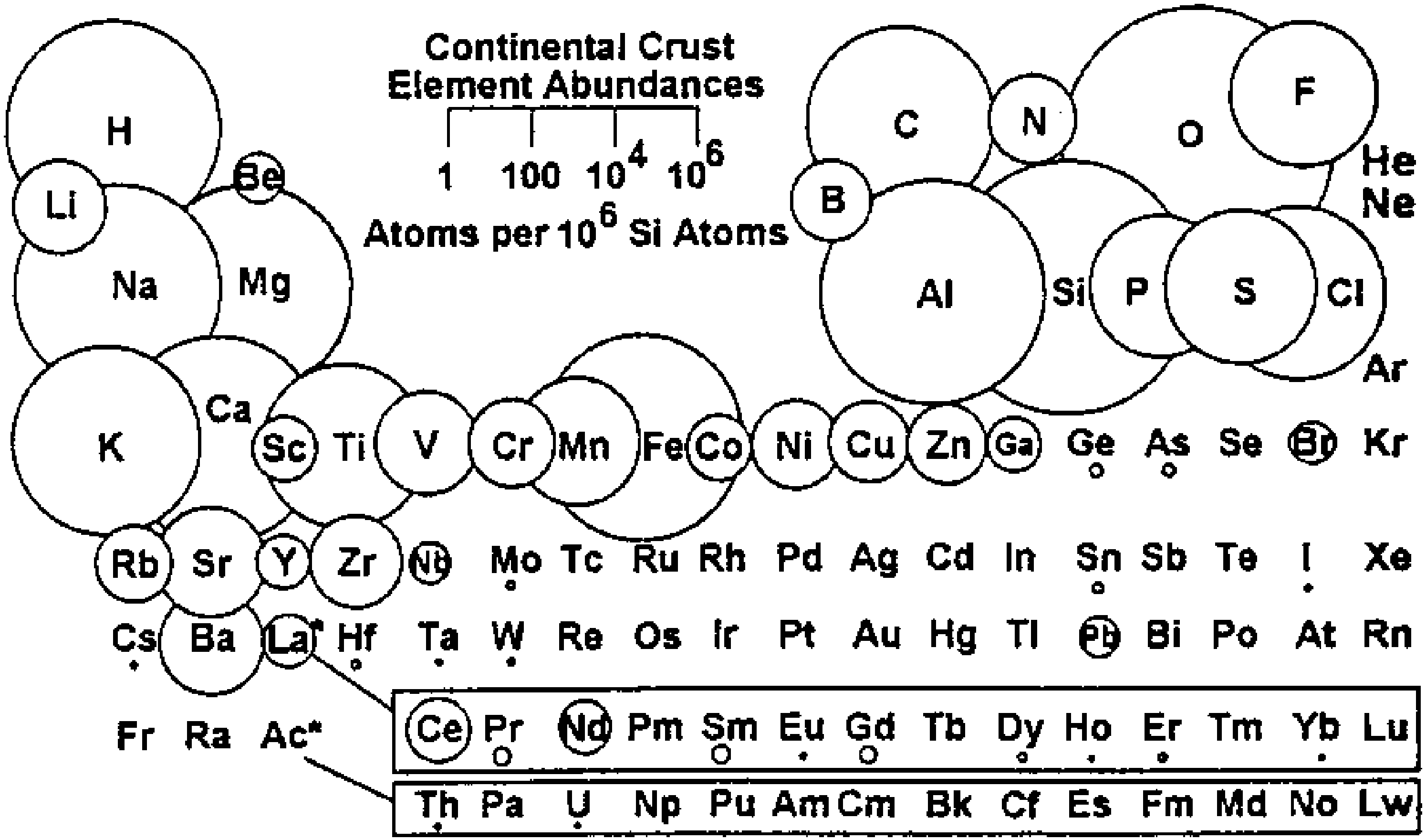
Lecture #27

Coordination Chemistry: Hydroxides & oxides

(Stumm & Morgan, Chapt.6: pg.272-275)

Benjamin; Chapter 8.1-8.6

Elemental abundance in crust



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

Zinc

- An essential metal
  - Needed for certain enzyme, e.g., alcohol dehydrogenase
  - Associate with a number of diseases
- Only one oxidation state (+2)
  - Electrons: $3d^{10}$, $4s^2$ (like Mg: $3s^2$)
- Uses in plumbing
  - Galvanized steel/iron – coat of Zn protects from oxidation
    - Now mostly for mains and connections, not premise
  - Copper Alloys
    - Brass (Cu, Zn & <2% Pb),
    - Bronze (Cu, ~12% Sn, & others)

Hydrolysis

- Metal accepts an electron from water and releases or repels a proton
  - Example: Zinc
    - First step
      - $Zn(H_2O)_6^{+2} = Zn(H_2O)_5OH^+ + H^+$

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

    - Second step
      - $Zn(H_2O)_5OH^+ = Zn(H_2O)_4(OH)_2^o + H^+$

$$ {}^*K_2 = \frac{[Zn(OH)_2][H^+]}{[ZnOH^+]} $$

Hydrolysis (cont.)

- Zinc example expressed as hydroxide formation
  - First step
    - $Zn(H_2O)_6^{+2} + OH^- = Zn(H_2O)_5OH^+ + H_2O$

$$K_1 = \frac{\left[Zn(OH)^+\right]}{[Zn^{+2}][OH^-]}$$

  - Second step
    - $Zn(H_2O)_5OH^+ + OH^- = Zn(H_2O)_4(OH)_2{}^o + H_2O$

$$K_2 = \frac{\left[Zn(OH)_2\right]}{[ZnOH^+][OH^-]}$$

Hydrolysis (cont.)

- Converting between the two forms

$Zn(H_2O)_6^{+2} + OH^- = Zn(H_2O)_5OH^+ + H_2O$

$H_2O = H^+ + OH^-$

$Zn(H_2O)_6^{+2} = Zn(H_2O)_5OH^+ + H^+$

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

$$K_w = [H^+][OH^-]$$

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

Cumulative stability constants

- β describes the equilibrium between any given complex and its component metal and ligands
  - is the product of the successive K's

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

  - Which describes the following equilibrium

$$Zn(H_2O)_6^{+2} + 2OH^- = Zn(H_2O)_4(OH)_2 + 2H_2O$$

Cumulative stability constants (cont.)

- And $^*\beta$ is the form of β which is in terms of H^+, rather than OH^-
  - is the product of the successive $^*K$'s

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

  - Which describes the following equilibrium

$$Zn(H_2O)_6^{+2} = Zn(H_2O)_4(OH)_2 + 2H^+$$

  - And:

$$^*\beta_2 = \beta_2 (K_w)^2$$

Cumulative stability constants (cont.)

- So, in general:

$$\beta_m = \prod_{x=1}^{x=m} K_x = \frac{\left[Me(OH)_m^{+(n-m)}\right]}{[Me^{+n}][OH^-]^m}$$

- And:

$$^*\beta_m = \prod_{x=1}^{x=m} {}^*K_x = \frac{\left[Me(OH)_m^{+(n-m)}\right]\left[H^+\right]^m}{[Me^{+n}]}$$

- To next lecture