EWCE 105
Environmental Chemistry

Lecture 8

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Lecture Outlines

Topics	Sub-Topics	References
Redox Equilibria	• Significance of redox equilibria in natural water • Development of pE concept, electron activity	1. **Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters** **Authors:** Werner Stumm and James J Morgan 3rd ed., Hoboken : Wiley, 2012

Redox Equilibria

- There is a conceptual analogy between acid-base and reduction-oxidation reactions.

- Acid – proton donors
- Base – proton acceptors
- Reductants – electron donors
- Oxidants – electron acceptors

- As there are no free electrons, every oxidation is accompanied by a reduction and vice versa.

- An oxidant is a substance that causes oxidation to occur while being reduced itself.

Redox Equilibria – Significance in Natural Water

- Redox phenomena are highly significant in the environmental chemistry of natural waters and wastewaters.

- For example, in a lake, the reduction of O_2 by organic matter (CH_2O) results in O_2 depletion, may cause fish kill.

$$\mathbf{CH_2O + O_2 = CO_2 + H_2O}$$

O_2 oxidize the organic matter and hence is being reduced itself

- The rate at which sewage is oxidized is crucial to the operation of a waste treatment plant.

Redox Equilibria – Significance in Natural Water

- Reduction of insoluble iron (III) to soluble iron (II) in a reservoir contaminates the water with dissolved iron, which is hard to remove in the water treatment plant.

$$Fe(OH)_3\,(s) + 3H^+ + e^- \longrightarrow Fe^{2+} + 3H_2O$$

- Oxidation of NH_4^+ to NO_3^- in water converts ammonium nitrogen to nitrate, a form more assimilable by algae in the water

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O$$

Electron Activity and pE

- Though aqueous solutions do not contain free protons and free electrons, it is possible to define relative proton and electron activities.

- pH [= - log {H+}] measures the relative tendency of a solution to accept or transfer protons.

- In an acid solution (proton donor) this tendency is low, while it is higher in alkaline solutions (proton acceptors).

Electron Activity and pE

- pE gives the electron activity at equilibrium and measures the relative tendency of a solution to accept or transfer electrons.

- pE = - log {e}

- In a highly reducing solution the tendency to donate electrons, i.e. the hypothetical “electron pressure” or electron activity is relatively large.

Electron Activity and pE

- Just as the activity of hypothetical hydrogen ions is very low at high pH, the activity of hypothetical electrons is very low at high pE.

- Thus a high pE indicates a relatively high tendency for oxidation (electron donation).