Updated: 16 September 2019

Print version

CEE 370 Environmental Engineering Principles

Lecture #5
Environmental Chemistry III:
Kinetics & Activity

Reading: Mihelcic & Zimmerman, Chapter 3

Davis & Masten, Chapter 2
Mihelcic, Chapt 3.1

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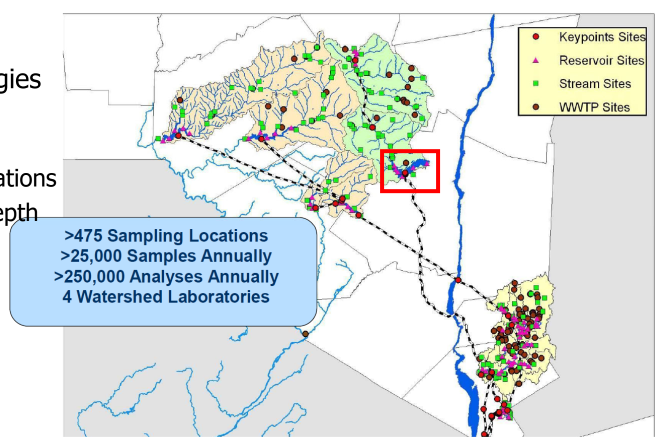
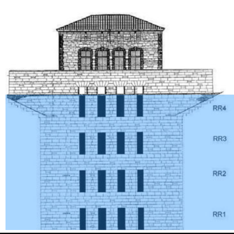
NYC Watershed Monitoring

- Operational Strategies
  - Select or bypass reservoirs
  - Select intake locations
  - Select optimal depth





From: Bader & Emery, WQTC, Nov 2015

Rondout Reservoir

- Fed by many streams of varying size

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Neversink River

waterdata.usgs.gov/ny/nwis/inventory/?site_no=01435000

USGS 01435000 NEVERSINK RIVER NEAR CLARYVILLE NY

Available data for this site SUMMARY OF ALL AVAILABLE DATA GO

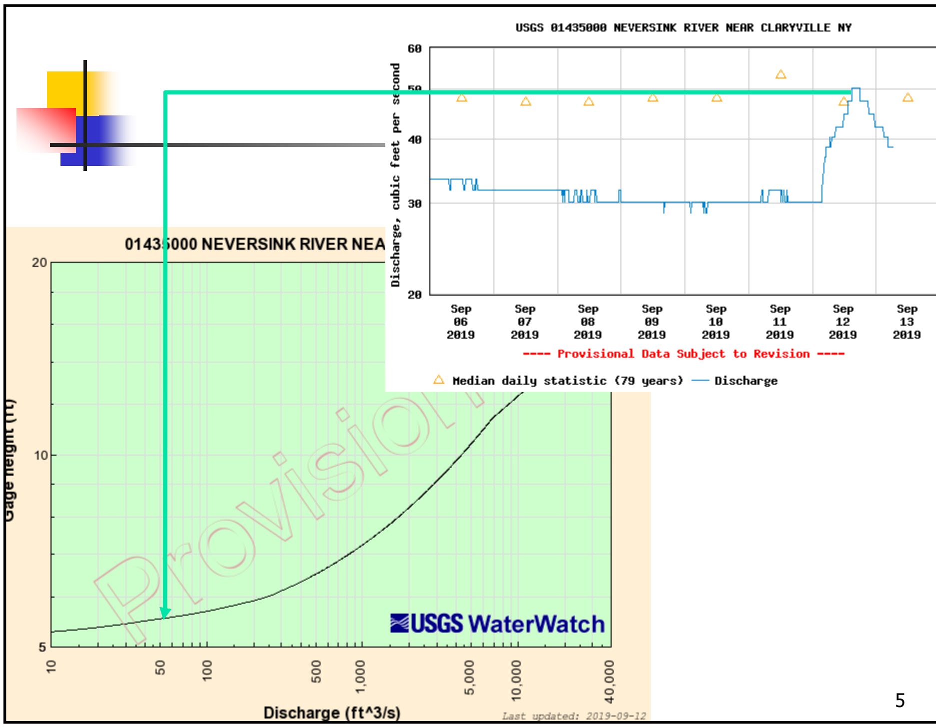
Stream Site

DESCRIPTION:

Latitude 41°53'24", Longitude 74°35'24" NAD83
Sullivan County, New York, Hydrologic Unit 02040104
Drainage area: 66.6 square miles
Datum of gage: 1,521.67 feet above NAVD88.

AVAILABLE DATA:

Data Type	Begin Date	End Date	Count
Current / Historical Observations (availability statement)	1987-04-01	2019-09-13	
Daily Data			
Temperature, water, degrees Celsius	2012-01-12	2019-09-12	8262
Discharge, cubic feet per second	1937-11-01	2019-09-12	29118
Daily Statistics			
Temperature, water, degrees Celsius	2012-01-12	2019-02-28	2554
Discharge, cubic feet per second	1937-11-01	2018-09-30	28772
Monthly Statistics			
Temperature, water, degrees Celsius	2012-01	2019-02	
Discharge, cubic feet per second	1937-11	2018-09	
Annual Statistics			
Temperature, water, degrees Celsius	2012	2019	
Discharge, cubic feet per second	1938	2018	
Peak streamflow	1938-07-22	2018-08-17	80
Field measurements	1950-11-25	2019-08-13	800
Field/Lab water-quality samples	1954-04-06	2019-08-06	1399
Water-Year Summary	2005	2018	14
Revisions	Available (site:1) (timeseries:0)		



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NYC & USGS

- adf

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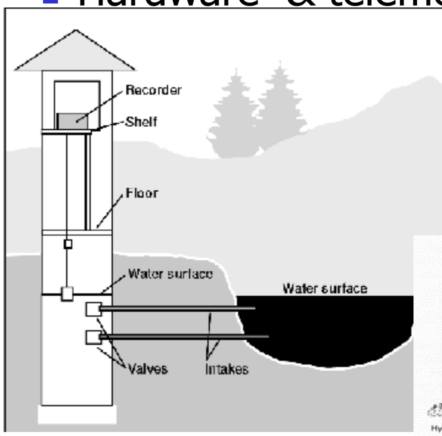
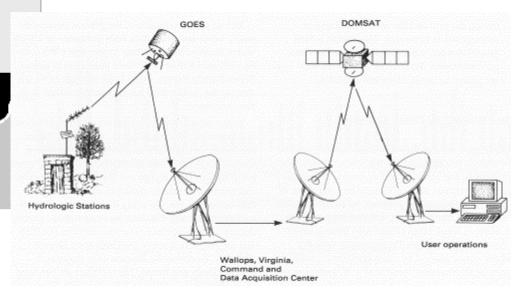
USGS Gaging Stations

- Hardware & telemetry





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Current Meter Deployment

- Current meter and weight suspended from a bridge crane
- Wading rod and current meter used for measuring the discharge of a river

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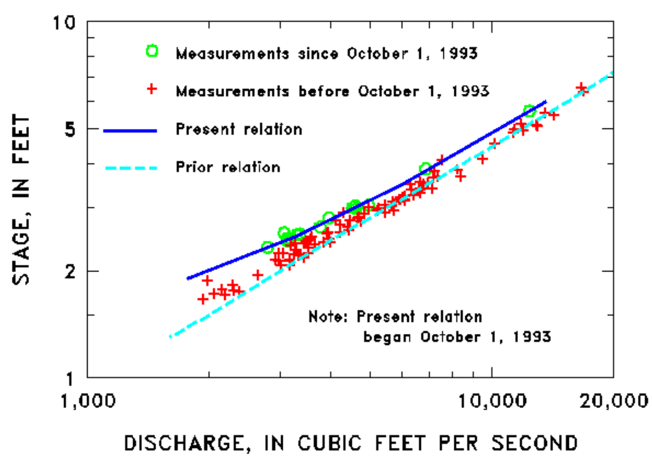
Electromagnetic sensors

- Hach FH950 flow r

Images: www.hach.com

Stage vs Discharge

- Sections of stage-discharge relations for the Colorado River at the Colorado--Utah State line



Wetlands (WOTUS)

- Protecting upland areas to protect downstream water

Friday, September 13, 2019 | DAILY HAMPSHIRE GAZETTE B3

Trump administration drops Obama-era water protection

Regulation covered upstream tributaries, wetlands

By JOHN FLESHER
Associated Press

TRAVERSE CITY, Mich. — The Trump administration revoked an Obama-era regulation Thursday that shielded many U.S. wetlands and streams from pollution but was opposed by developers and farmers who said it hurt economic development and infringed on property rights.

Environmental groups criticized the administration's action, the latest in a series of moves to roll back environmental protections put into place under President Barack Obama.

The 2015 Waters of the United States rule defined the waterways subject to federal regulation. Scrapping it "puts an end to an egregious power grab, eliminates an ongoing patchwork of clean water regulations and restores a longstanding and familiar regulatory framework," Environmental Protection Agency chief Andrew Wheeler said at a news conference in Washington, D.C.

Wheeler and R.D. James, assistant secretary of the Army for civil works, signed a document overturning the rule and temporarily restoring an earlier regulatory system that emerged after a 2006 ruling from a sharply divided Supreme Court.

The agencies plan to adopt a new rule by the end of the year that will define protected waterways more narrowly than the Obama policy.

The Clean Water Act requires landowners to obtain federal permits before developing or polluting navigable waterways such as rivers and lakes. But disputes have long persisted over what other waters are subject to regulation — particularly wetlands that don't have a direct connection to those larger waters, plus small headwater streams and channels that flow only during and after rainfall.

Environmentalists contend many of those smaller, seemingly isolated waters are tributaries of the larger waterways and can have a significant effect on their quality. Denying them federal protection would leave millions of Americans with less safe drinking water and allow damage of wetlands that prevent flooding, filter pollutants and provide habitat for a multitude of fish, waterfowl and other wildlife, they said.

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- Protecting the natural resources

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Common Constituents

- N, P, and S containing compounds are often expressed in terms of their elemental concentration
- Examples
  - 66 mg of $(NH_4)_2SO_4$ added to 1 L of water
  - 85 mg of $NaNO_3$ added to 1 L of water

See also example 2.13, on pg. 51 of Mihelcic & Zimmerman

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Example

- Consider a solution of Ammonium Sulfate prepared by dissolving 66 g of the anhydrous compound in water and diluting to 1 liter. What is the concentration of this solution in:
  - a) g/L?
  - b) moles/L?
  - c) equivalents/L?
  - d) g/L as sulfate?
  - e) g/L as N?

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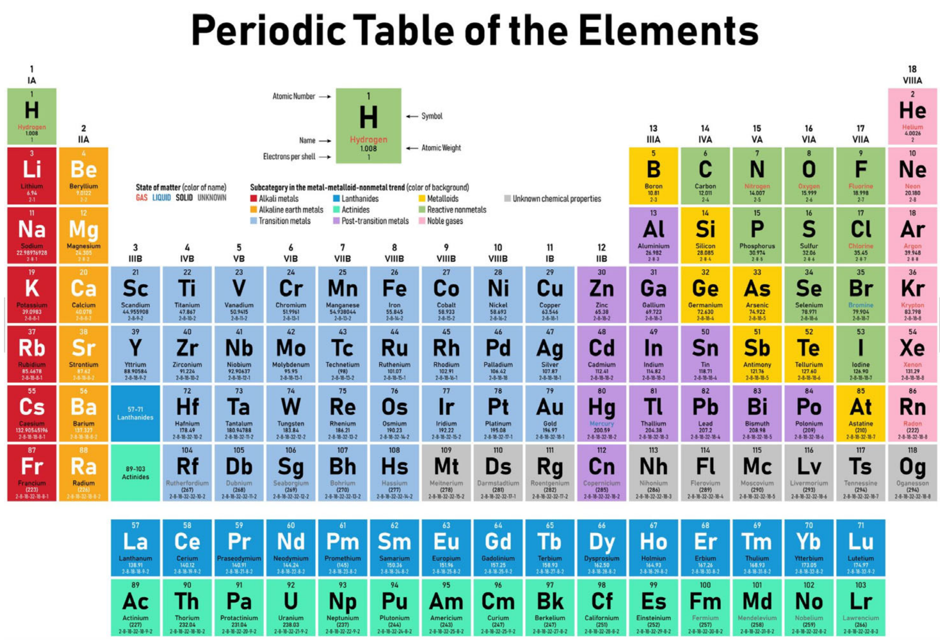

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- a) 66 g/L
- b) The gram formula weight of ammonium sulfate is 132 g/mole. So, using equation 2.7, on gets:
  - Molarity = (66 g/L)/(132 g/mole) = 0.5 moles/L or 0.5 M.
- c) Without any specific information regarding the use of this solution, one might simply presume that either the sulfate group or the ammonium group will be the reacting species. In either case, Z should be equal to two (product of the oxidation state times the number of groups). So:
  - Normality = 0.5 moles/L * 2 equivalents/mole
  - = 1 equivalent/L or 1.0 N or N/1.

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- d) The GFW for sulfate is:
  - GFW = 32 + 4*16 = 96.
  - The molarity of sulfate is:
    - Molarity = 0.5 moles-$(NH_4)_2SO_4$/L * 1 mole-SO_4/mole-$(NH_4)_2SO_4$
    - = 0.5 moles-SO_4/L
  - Then, one gets:
    - mass/L = Molarity * GFW = 0.5 moles-SO_4/L * 96 g-SO_4/mole-SO_4
    - = 48 g-SO_4/L

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- e) The GFW for nitrogen is simply 14:
  - The molarity of nitrogen is:
    - Molarity = 0.5 moles-$(NH_4)_2SO_4$/L * 2 moles-N/mole-$(NH_4)_2SO_4$
    - = 1 mole-N/L
  - Again, one gets:
    - mass/L = Molarity * GFW = 1 mole-N/L * 14 g-N/mole-N
    - = 14 g-N/L or 14 g NH_3-N/L

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Calcium carbonate units

- Used for major ion concentrations in drinking waters
  - Alkalinity
  - Hardness
- Since $CaCO_3$ is divalent (Z=2) and its GFW is 100 g, its GEW is 50 g
  - 50 g/equivalent or 50 mg/meq
  - 50,000 mg/equivalent

See also example 2.14, on pg. 52 of Mihelcic & Zimmerman

Ionic Substances

- Properties in water
  - One part of molecule (the "metal", forming a cation) entirely gives up an electron to the other (forming an anion)
  - Frequently these contain alkali metals or halogens: disparate electronegativities
- Examples
  - Simple salts: NaCl, KNO_3
  - Strong acids/bases: HCl, HNO_3, NaOH

- Gas samples (compressible)

$$\frac{0.056mg\ \text{Ozone}}{1m^3\ \text{air}}$$

  - Could be converted to a ppm_m basis
    - But this would change as we compress the air sample
  - Could also be converted to a ppm_v basis
    - Independent of degree of compression
    - But now we need to convert mass of ozone to volume of ozone

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Ideal Gas Law

By definition:

$$n = \frac{mass(g)}{GFW}$$

- An ideal gas
  - Will occupy a certain fixed volume as determined by:

$$PV = nRT$$

$$V = n\frac{RT}{P} = \frac{mass(g)}{GFW}\frac{RT}{P}$$

regardless of the nature of the gas

$\frac{RT}{P}$ =22.4 L at 1 atm, 273.15ºK

  - Where:
    - P=pressure
    - V=volume
    - n=number of moles
    - T=temp
    - R=universal gas constant=0.08205 L-atm/mole-ºK
    - GFW=gram formula weight

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Convert mass to moles

- Now we know that ozone's formula is O_3
  - Which means it contains 3 oxygen atoms
  - Therefore the GFW = 3x atomic weight of oxygen in grams or 48 g/mole

$$\frac{0.056mg \text{ Ozone}}{1m^3 \text{ air}}$$

- n=mass(g)/GFW
- n=0.056x10^{-3}g/(48g/mole)
- n=0.00117x10^{-3} moles

$$\frac{0.00117x10^{-3} moles \text{ Ozone}}{1m^3 \text{ air}}$$

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Now determine ppm$_v$

$$ppm_v = \frac{volume_{ozone}}{volume_{air}}$$

$$= \frac{0.00117x10^{-3} moles\ x22.4L/mole}{1m^3 \text{ air}}$$

$$= \frac{0.026x10^{-3} \text{ L Ozone}}{1x10^3 \text{ L air}}$$

$$= 0.026 \text{ ppm}_v \text{ O}_3 \text{ in air}$$

$$= 26 \text{ ppb}_v \text{ O}_3 \text{ in air}$$

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Mole & volume fractions

$$\frac{V_i = n_i \frac{RT}{P}}{V_{total} = n_{total}\frac{RT}{P}}$$

- Based on the ideal gas law:
  - The volume fraction (ratio of a component gas volume to the total volume) is the same as the mole fraction of that component
  - Therefore: $\frac{V_i}{V_{total}} = \frac{n_i}{n_{total}}$

Defined as: Volume fraction ($\frac{V_i}{V_{total}}$)

Defined as: mole fraction ($\frac{n_i}{n_{total}}$)

  - And since the fraction of the total is one-millionth of the number of ppm: $10^{-6}\, ppm_v \equiv \frac{V_i}{V_{total}} = \frac{n_i}{n_{total}}$

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Partial pressures

$$PV = nRT$$

$$P = \frac{n}{V}RT$$

- Based on the ideal gas law:
  - And defining the partial pressure (P_i) as the pressure a component gas (i) would exert if all of the other component gases were removed.
  - We can write: $P_i = \frac{n_i}{V_{total}}RT$ and $P_{total} = \frac{n_{total}}{V_{total}}RT$
  - Which leads to: $\frac{P_i}{P_{total}} = \frac{n_i}{n_{total}}$
  - And: $P_i = P_{total}\frac{n_i}{n_{total}} = P_{total}10^{-6}\, ppm_v$

Try example 2.6, on pg. 47 of Mihelcic & Zimmerman

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Earth's Atmosphere

Divide by 100 and you get the partial pressure for a total pressure of 1 atm.

Table 2-2. Composition of the Atmosphere*

Compound	Concentration (% volume or moles)	Concentration (ppm_V)
Nitrogen (N_2)	78.1	781,000
Oxygen (O_2)	20.9	209,000
Argon (Ar)	0.93	9,300
Carbon dioxide (CO_2)	0.035	350
Neon (Ne)	0.0018	18
Helium (He)	0.0005	5
Methane (CH_4)	0.00017	1.7
Krypton (Kr)	0.00011	1.1
Hydrogen (H_2)	0.00005	0.500
Nitrous oxide (N_2O)	0.000032	0.316
Ozone (O_3)	0.000002	0.020

GHGs; increasing

Data from Graedel and Crutzen, 1993.
*Values represent concentrations in dry air at remote locations.

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Greenhouse Gases

Compound	CO_2e Multiplier	2011 level	CO_2e
Carbon dioxide (CO_2)	1	391 ppm	391 ppm
Methane (CH_4)	25	1,813 ppb	45 ppm
Nitrous Oxide (N_2O)	298	324 ppb	97 ppm
Hydrofluorocarbons ($C_xH_aF_yO_z$)	124-14,800		
Perfluorocarbons ($C_xF_yO_z$)	7,390-12,200		
Sulfur Hexafluoride (SF_6)	22,800		

Compare with tables 2.2 and 2.4 in M&Z

CO_2e = greenhouse gas equivalents in units of carbon dioxide

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Stoichiometry

$$2\,H_2 \;+\; O_2 \;\Leftrightarrow\; 2\,H_2O$$

$$2\,H_2 \;+\; O_2 \;\leftrightarrow 2\,H_2O$$
$$2\;moles\;\;H_2 \;+\; 1\;mole\;\;O_2 \;\leftrightarrow\; 2\;moles\;\;H_2O$$
$$(2\;x\;2\;x\;1.008\;g) \;+\; (1\;x\;2\;x\;16.00\;g) \;=\; (2\;x\;18.016\;g)$$

Law of ***definite proportions*** or ***constant composition***

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Neutralization Example

A tractor trailer truck with a full load of hydrochloric acid (40,000 lbs) crashes into a bridge, spilling the acid into the stream. How much lime [$Ca(OH)_2$] is required to neutralize the acid? The neutralization reaction is:

$$2HCl + Ca(OH)_2 = CaCl_2 + 2H_2O$$

Example 4.8 from Ray

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Solution to Neutralization Ex.

Determine the number of moles of hydrochloric acid:

$$M_{HCl} = 40{,}000 \text{ lbs x } \frac{454 \text{ g}}{1 \text{ lb}} \text{ x } \frac{1 \text{ mole}}{36.5 \text{ g}} = 5.0 \text{ x } 10^5 \text{ moles HCl}$$

From the stoichiometric formula, one mole of lime neutralizes two moles of hydrochloric acid. The required amount of lime is then:

$$M_{Ca(OH)_2} = 5.0 \text{ x } 10^5 \text{ moles HCl x } \frac{1 \text{ mole } Ca(OH)_2}{2 \text{ moles HCl}} = 2.5 \text{ x } 10^5 \text{ moles } Ca(OH)_2$$

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Solution (cont.)

The mass of lime required is:

$$M_{Ca(OH)_2} = 2.5 \text{ x } 10^5 \text{ moles } Ca(OH)_2 \text{ x } \frac{74 \text{ g } Ca(OH)_2}{1 \text{ mole } Ca(OH)_2} = 1.8 \text{ x } 10^4 \text{ Kg}$$

$$M_{Ca(OH)_2} = 41{,}000 \text{ lb } Ca(OH)_2$$

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Acetic Acid Example

Acetic acid [CH_3COOH] or vinegar is oxidized to carbon dioxide and water by microbial action. A vinegar manufacturing plant has 50 mg/L of acetic acid in its effluent wastewater. The plant flow is 500 m^3 per day. How much oxygen is required each day to oxidize the vinegar?

First the equation must be balanced:

$$CH_3COOH + 2O_2 \leftrightarrow 2CO_2 + 2H_2O$$

Thus, two moles of oxygen are required to oxidize the acetic acid to carbon dioxide and water. The amount of acetic acid to oxidize each day is:

Example 4.9 from Ray

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Solution to Acetic Acid Ex.

$$M_{HAc} = 50 \frac{mg\ HAc}{L} \times \frac{g}{1000\ mg} \times 500 \frac{m^3}{day} \times \frac{1000\ L}{1\ m^3} \times \frac{1\ mol\ HAc}{60\ g\ HAc}$$

$$M_{HAc} = 417 \frac{mol}{d}$$

Since two moles of oxygen are required for each mole of acetic acid, the required oxygen is:

$$M_{O_2} = 417 \frac{mol\ HAc}{day} \times \frac{2\ mol\ O_2}{mol\ HAc} = 834 \frac{mol\ O_2}{day}$$

The mass of oxygen is then:

$$M_{O_2} = 834 \frac{mol\ O_2}{day} \times \frac{32\ g\ O_2}{mol\ O_2} = 26{,}700 \frac{g\ O_2}{day}$$

$$M_{O_2} = 26.7 \frac{Kg\ O_2}{day}$$

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Oxygen Demand

- **Theoretical oxygen demand** (or **ThOD)** is the amount of oxygen required to convert the material to carbon dioxide and water. In cases where the organic matter contains amine compounds [$-NH_2$], the end product of the nitrogen is ammonia [NH_3].
- **Biochemical Oxygen Demand** (or **BOD**) is the amount of oxygen consumed by microorganisms in converting all biodegradable organic matter to carbon dioxide, water and ammonia
- **Chemical Oxygen Demand** (or **COD**) is the amount of strong oxidant (in oxygen equivalents) consumed in the course of converting aqueous substances to carbon dioxide, water and ammonia

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ThOD Example

Ethanol or ethyl alcohol is used in beverages, as a gasoline additive, and other industrial applications. Small amounts of ethanol and also sugar, are used in the biological process to produce methanol. Both these compounds inevitably end up in the wastewaters coming from facilities which produce methanol. Calculate the theoretical oxygen demand for a wastewater containing:

a) 25 mg/L ethanol [CH_3CH_2OH]
b) 45 mg/L glucose [$C_6H_{12}O_6$]
c) A mixture of 25 mg/L ethanol and 45 mg/L sucrose

Example 4.10 from Ray

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Solution to ThOD Example

a) The first step is to balance the oxidation of ethanol (often written EtOH) to end products of carbon dioxide and water.

$$CH_3CH_2OH + \underline{3}\,O_2 \rightarrow \underline{2}\,CO_2 + \underline{3}\,H_2O$$

GFW=46 GFW=96

$$ThOD = 25\frac{mg\ EtOH}{L} \times \frac{96\ mg\ O_2}{46\ mg\ EtOH}$$

$$ThOD = 52\ mg\ O_2/L$$

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Solution (cont.)

b) As with the ethanol in part a) above, the first step is to write the balanced equation for the oxidation of glucose to end products of carbon dioxide and water.

$$C_6H_{12}O_6 + \underline{6}\,O_2 \rightarrow \underline{6}\,CO_2 + \underline{6}\,H_2O$$

GFW=180 GFW=192

$$ThOD = 45\frac{mg\ C_6H_{12}O_6}{L} \times \frac{192\ mg\ O_2}{180\ mg\ C_6H_{12}O_6}$$

$$ThOD = 48\ mg\ O_2/L$$

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Solution (cont.)

c) The ThOD of the mixture is simply the sum of the ThOD's of the individual components, or:

$$ThOD_{tot} = 52 \text{ mg } O_2/L + 48 \text{ mg } O_2/L$$

$$ThOD_{tot} = 100 \text{ mg } O_2/L$$

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Reactions & Stoichiometry

- Balancing chemical equations
  - Acid-Base
    - $Ca(HCO_3)_2 + NaOH = Ca(OH)_2 + NaHCO_3$
  - Oxidation of iron
    - $O_2 + Fe^{+2} = Fe^{+3} + H_2O$
  - Precipitation of alum
    - $Al_2(SO_4)_3 + H_2O = Al(OH)_3$
  - Quenching of chlorine with thiosulfate
    - $HOCl + Na_2S_2O_3 = HCl + Na_2S_4O_6$

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Redox (oxidation-reduction) reactions

- Involve transfer of electrons between chemical species
  - Consider the reaction between A & B

$$A_{ox} + B_{red} \rightarrow A_{red} + B_{ox}$$

  - Now looking more closely at what happens

$$A_{ox} + e^{-} \rightarrow A_{red}$$ ⟵ Reduction half reaction

$$B_{red} \rightarrow B_{ox} + e^{-}$$ ⟵ Oxidation half reaction

- Which also results in a change in oxidation state

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Oxidation State

- Oxidation state is characterized by an oxidation number
  - the charge one would expect for an atom if it were to dissociate from the surrounding molecule or ion (assigning any shared electrons to the more electronegative atom).
  - may be either a positive or negative number, usually, an integer between -VII and +VII
- Rules for calculating oxidation state
  - The overall charge on a molecule or ion is equal to the sum of the oxidation states of each atom within
  - Some atoms are nearly always at the same oxidation state:
    - Hydrogen is almost always plus one (+I)
    - Oxygen is almost always negative two (-II)

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Oxidation States

Stumm & Morgan, 1996; Table 8.1, pg. 427

Table 8.1. Oxidation State

Rules for Assigning Oxidation States:

(1) The oxidation state of a monoatomic substance is equal to its electronic charge.
(2) In a covalent compound, the oxidation state of each atom is the charge remaining on the atom when each shared pair of electrons is assigned completely to the more electronegative of the two atoms sharing them. An electron pair shared by two atoms of the same electronegativity is split between them.
(3) The sum of oxidation states is equal to zero for molecules, and for ions is equal to the formal charge of the ions.

Examples:

Nitrogen Compounds		Sulfur Compounds		Carbon Compounds	
Substance	Oxidation States	Substance	Oxidation States	Substance	Oxidation States
NH_4^+	N = −III, H = +I	H_2S	S = −II, H = +I	HCO_3^-	C = +IV
N_2	N = 0	$S_8(s)$	S = 0	HCOOH	C = +II
NO_2^-	N = +III, O = −II	SO_3^{2-}	S = +IV, O = −II	$C_6H_{12}O_6$	C = 0
NO_3^-	N = + V, O = −II	SO_4^{2-}	S = +VI, O = −II	CH_3OH	C = −II
HCN	N = −III, C = +II, H = +I	$S_2O_3^{2-}$	S = +II, O = −II	CH_4	C = −IV
SCN^-	S = −I, C = +III, N = −III	$S_4O_6^{2-}$	S = +2.5, O = −II	C_6H_5COOH	C = −2/7
		$S_2O_6^{2-}$	S = +V, O = −II		

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Balancing Equations

- The first step in working with oxidation reactions is to identify the role of the reacting species.
  - At least one reactant must be the oxidizing agent (i.e., containing an atom or atoms that become reduced)
  - At least one must be a reducing agent (i.e., containing an atom or atoms that become oxidized).
- The second step is to balance the gain of electrons from the oxidizing agent with the loss of electrons from the reducing agent.
- Next, oxygen atoms are balanced by adding water molecules to one side or another and hydrogens are balanced with H^+ ions.

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Balancing Equations

$Al_2(SO_4)_3 + xH_2O = yAl(OH)_3 + zSO_4 + mH^+$

- What is the value of "y"?
  A. 0.5
  B. 1
  C. 2
  D. 3
  E. None of the above

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Balancing Equations

$Al_2(SO_4)_3 + xH_2O = 2Al(OH)_3 + zSO_4 + mH^+$

- What is the value of "z"?
  A. 0.5
  B. 1
  C. 2
  D. 3
  E. None of the above

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Balancing Equations

$Al_2(SO_4)_3 + xH_2O = 2Al(OH)_3 + 3SO_4 + mH^+$

- What is the value of "x"?
  - A. 0.5
  - B. 1
  - C. 2
  - D. 3
  - E. None of the above

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Balancing Equations

$Al_2(SO_4)_3 + 6H_2O = 2Al(OH)_3 + 3SO_4^{-2} + mH^+$

- What is the value of "m"?
  - A. 1
  - B. 3
  - C. 6
  - D. 12
  - E. None of the above

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Balancing Equations

$$Al_2(SO_4)_3 + 6H_2O = 2Al(OH)_3 + 3SO_4^{-2} + 6H^+$$

- Now make sure everything balances
  - Each element
  - Charges

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Oxidation of Iron by Oxygen

$$xO_2 + 1Fe^{+2} + mH^+ = yFe^{+3} + zH_2O$$

- What is the value of "x"?
  A. 0.25
  B. 0.5
  C. 1
  D. 2
  E. Can't tell

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Oxidation of Iron by Oxygen

$\frac{1}{4}O_2 + 1Fe^{+2} + 1H^{+} = 1Fe^{+3} + \frac{1}{2}H_2O$

- What is the value of "x"?
  - A. 0.25
  - B. 0.5
  - C. 1
  - D. 2
  - E. Can't tell

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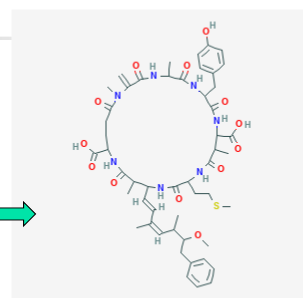
sulfur

- In some amino acids
  - Methionine, Cysteine
- Microcystin YM



  - Produced by Microcystis
- Exists in many oxidation states
  - Low oxidation states are often toxic
    - Hydrogen sulfide (H_2S)

Substance	Oxidation States
H_2S	S = −II, H = +I
$S_8(s)$	S = 0
SO_3^{2-}	S = +IV, O = −II
SO_4^{2-}	S = +VI, O = −II
$S_2O_3^{2-}$	S = +II, O = −II
$S_4O_6^{2-}$	S = +2.5, O = −II
$S_2O_6^{2-}$	S = +V, O = −II

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Tom vs Miocrocystis

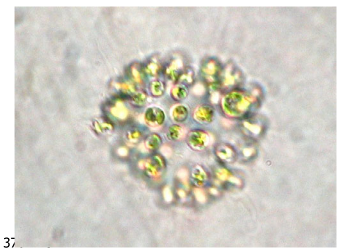
Tom Brady

- No ability to produce toxins

Microcystis aeruginosa

- Can make many types of cyanotixins

Tom	1	0								1
Microcystis	1	1								2



CEE 37

Balancing equations: Redox

- Oxidation of hydrogen sulfide by chlorine

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- To next lecture