2005. 1. 17~19. for Lectures in Vietnam (by Jaeweon Cho, GIST)

Lecture Contents

Lecture 1: Water Treatment Chemistry

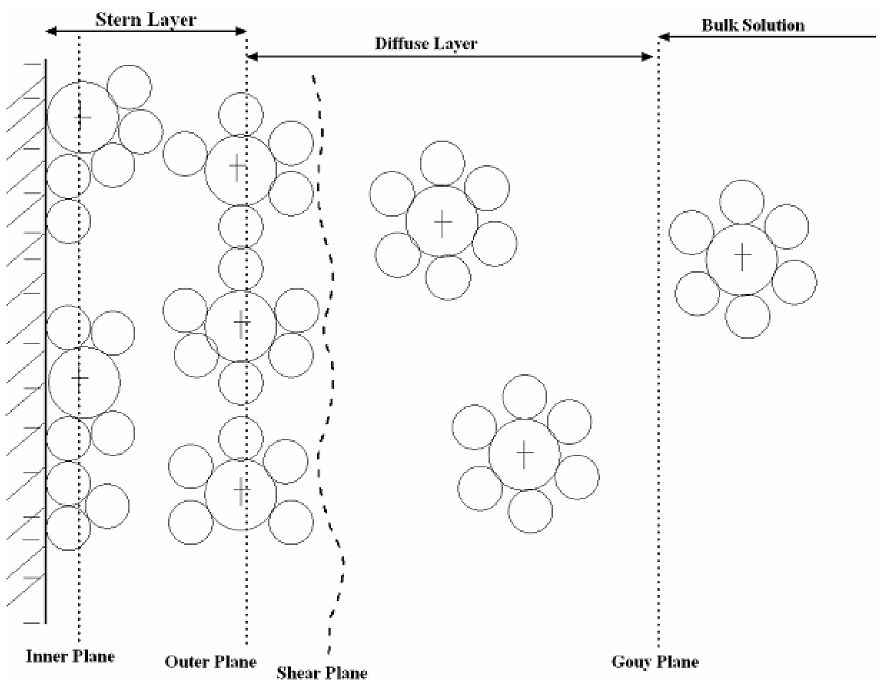
Flocculation/coagulation in Water Treatment

Turbidity 0.5 NTU; 0.1 NTU even lower

Turbidity is not everything any longer, but still important.

- Types of Colloids
  - Simple clay: kaolinite, montmorillonite; pH_{pzc} = 2.5, 4.6
  - Metal oxides: Al_2O_3, Fe_2O_3; $pH_{pzc} \approx 8.0$
  - Bio-colloids, bioparticles; generally negative, ex. pH_{pzc} for virus ≈ 5.0
  - NOM; meq/g → What is Natural Organic Matter? Why do we care about this?

- Surface chemistry configuration



Stern Model

Coagulation with alum:

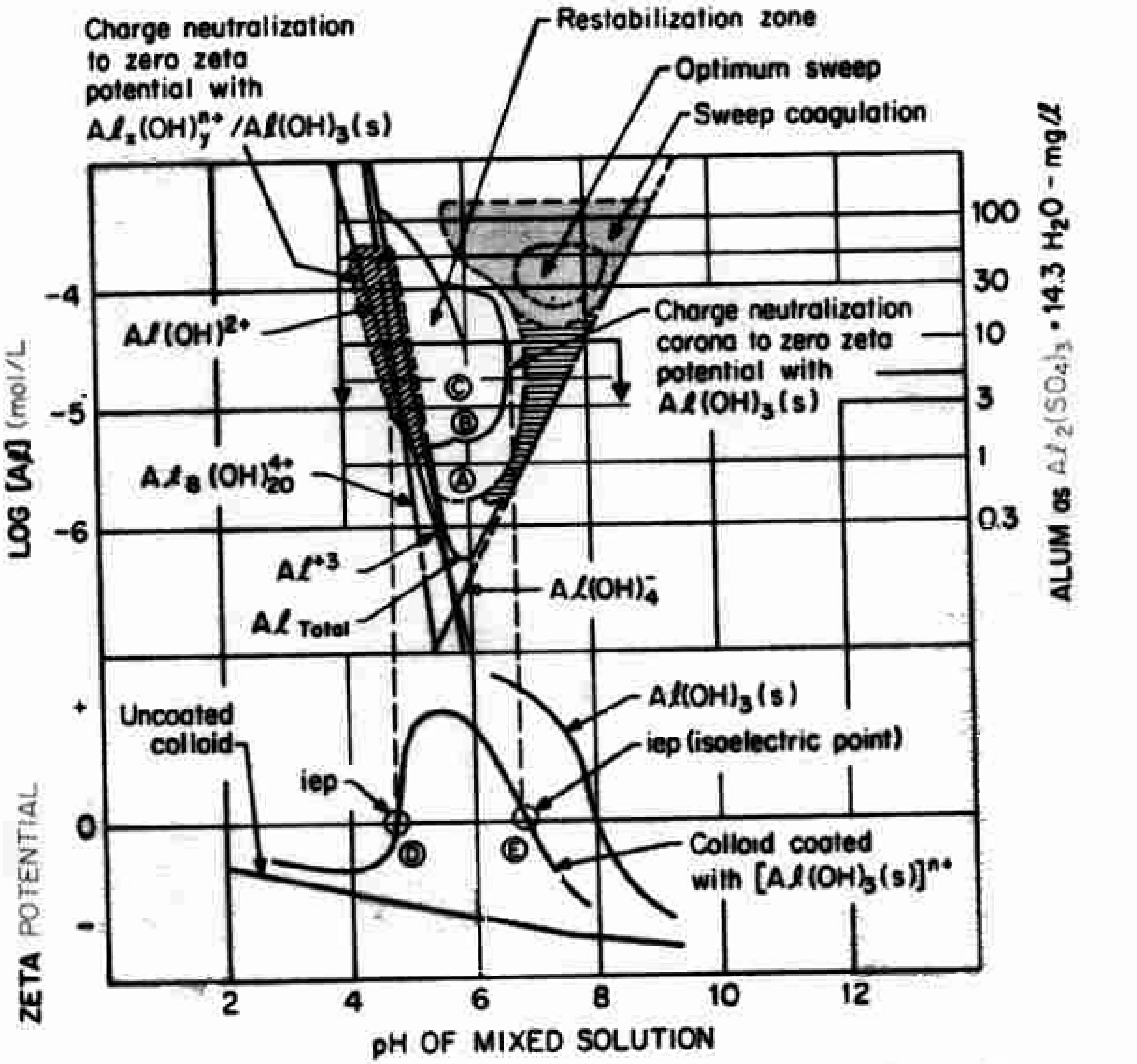


Figure 6.12 The alum coagulation diagram and its relationship to zeta potential.

- Factors influencing coagulation
    - Type of coagulant
    - Coagulant dose
    - pH
    - Nature and concentration of turbidity: sup-µm is more easy to remove than sub-µm
    - Alkalinity
    - Mixing
    - Temperature influence: need more coagulant in cold weather

- For NOM removal:
    - Generally, occurs through formations of Al-humate or Fe-humate precipitates
    - often with cationic polyelectrolyte
    - efficient for color removal; color resulted from ?
    - very sensitive in pH changes
    - 10% - 60% removals; source waters depending process
    - Enhanced coagulation

Disinfection

■ Objectives:
    - Inactivation of microbes at plants, and provision of residual within distribution system
    - Destruction of pathogens
    - Pathogenic bacteria (Salmonella typhosa) and viruses (e.g., Coxsackie)
    - Pathogenic protozoa: e.g., Giardia lamblia, Cryptosporidium
  - Indicator organism: Coliform bacteria, MCL$\leq$1/100 mL, not indicator of protozoa and virus
    - Proposed MCLs: 0 for coliform, viruses, and Giardia

■ Chemical disinfectants employed
    - Chlorine, Cl_2
    - Ozone, O_3
    - Chlorine dioxide, ClO_2
    - Chloramines, NH_2Cl: good residual, almost never disappear.
    - UV light, less by-products and costs, no residual.

■ Chemistry of chlorine:
    - $Cl_2 + H_2O \dashrightarrow HOCl + Cl^-$ (hypochlorous acid)
    - $HOCl \leftrightarrow H^+ + OCl^-$ (hypochlorite ion)

    pKa = 2.5×10^{-8} @25℃

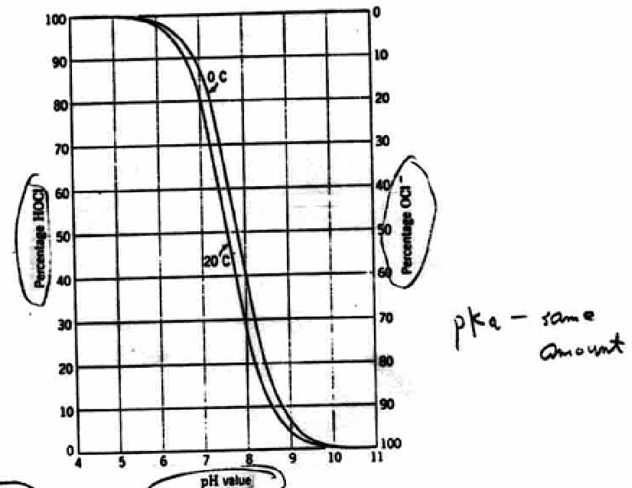


Fig. 31-5. Distribution of hypochlorous acid and hypochlorite ion in water at different pH values and temperatures. (After Morris, Sec. 31-11, footnote 14.)

- Free chlorine : $HOCl + OCl^-$
    - pH affects distribution
    - Biocidal efficiency: $HOCl > OCl^-$
    - Sodium hypochlorite: NaOCl (concentrated bleach)
    - Chlorine demand: Fe^{2+}, Mn^{2+}, H_2S, etc.
    - Chlorination by-products (DBPs): THMs, TOX, HAAs
    - THM formation:
        - Humic/Fulvic acids + Cl_2 --> $CHCl_3$
        - Br^- + Cl_2 --> Br_2: Bromine is much more substitution agent,
          Br --(approx. 50%)--> Org-Br
        - Humic/Fulvic + Br_2 --> $CHBr_3$
        - MCL = 80 μg/L
        - THMFP (96 hrs.) vs. SDS-THMs (24 hrs.), and instantaneously THMs
    - HAA formation:
        - Possibly humic/fulvic acids as well as hydrophilic NOM as well
        - $HAAFP_{maximum}$ = approx. 150-200 μg/L for Nakdong River (recall, MCL = just 60 --> 40 μg/L at the next year)

■ Factors affecting disinfection:
- Organism to be inactivated (type and density)
- Chemical disinfection (type and concentration)
- Disinfection-demanding substances
- Other water quality conditions: turbidity, pH, temperature (can be easily disinfected in high temperature than low temp.)

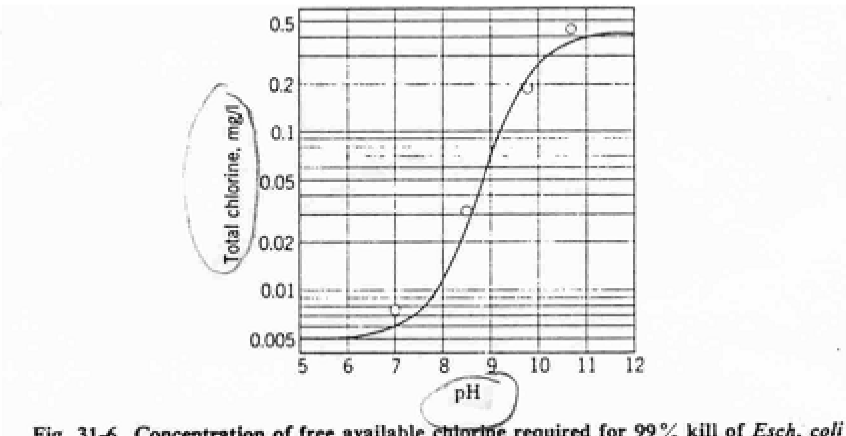


Fig. 31-6. Concentration of free available chlorine required for 99% kill of *Esch. coli* in 30 min at 2 to 5 C.

Cl_2 for (99% kill) function of pH

■ Alternative disinfectants:
- Monochloramine, NH_2Cl (=combined chlorine, not a free chlorine, free chlorine = $HOCl + OCl^-$) : with addition of sodium ammonia.

- Ozone:
  - $Br^- + O_3$ --> BrO_3^- (bromate, 10 μg/L) @ typically high pH
    --> Br_2 (bromine) to produce bromoform @ typically low pH
    - Organic aldehyde (e.g., formaldehyde): indirectly influence biodegradable effect (not that much health influencing)

■ Chemistry of chloramines:
- $HOCl + NH_3$ --> $NH_2Cl + H_2O$ (monochloramine)
- at higher ratio of NH_3/HOCl, $NHCl_2$ (dichloramine)

■ Biocidal efficiency:
- HOCl > OCl^- > NH_2Cl

■ Ozone:
- O_3 --> O_2
- O_3 --> $OH^{\cdot}$ (hydroxyl radical) at high pH
- Advantages:
  - effective bactericide and virucide
  - no halogenated DBPs (except $CHBr_3$ when Br^-)
  - powerful oxidant
    - as a pre-oxidant: T & O, microflocculation, THM precursor oxidation, color removal
  - Disadvantages:
    - Short half life: poor residual characteristics
    - By-products (formaldehyde)
    - Cost
    - On-site production
    - pH effects: O_3 vs. $OH^{\cdot}$ at high pH
  - Typical doses
    - Disinfection: 0.5 - 5.0 mg/L
    - THM precursor control: O_3/DOC = 0.5 - 2.0 mg/mg
    - Microflocculation; O_3/DOC = 0.2 mg/mg
  - Typical contact time: 5 - 10 minutes
  - CT = (Concentration of Ozone in effluent) × (contact time, t_{10})
    t_{10} : the time when 10% of water is disinfected (plug flow has this much credit, t_{10} approx. = t_{50})

■ Chlorine dioxide, ClO_2
- Produced from sodium chlorite and chlorine:
  $ClO_2 + H_2O$ --> $HClO_2$ (chlorous acid) + $HClO_3$ (chloric acid)
- Advantages:
  - no halogenated DBPs
  - longer residual than Cl_2
- Disadvantages:

- Chlorite ions, ClO_2^- (1 mg/L) and cost

- Biocidal efficiency: between HOCl and OCl^-

■ Chloramines:

Chloramines have recently been adopted by a number of utilities as a post-disinfectant. While it is much less reactive in forming THMs, it nevertheless still forms significant amounts of TOX, indicative of DBPs in general. Moreover, it is inferior in comparison to chlorine as a biocide, causing some concern about the microbiological quality of distribution systems.

- Chloramination alternatives:
  - NH_3 followed by Cl_2 (not easy to satisfy required CT value)
  - Cl_2 followed by NH_3 (maximizes disinfection, minimizes DBPs)
  - Preformed NH_2Cl

■ Summary

Disinfectant	Biocide	Residual	Cost
O_3	1	4	
ClO_2	2	2	
Cl_2	3	3	1
NH_2Cl	4	1	

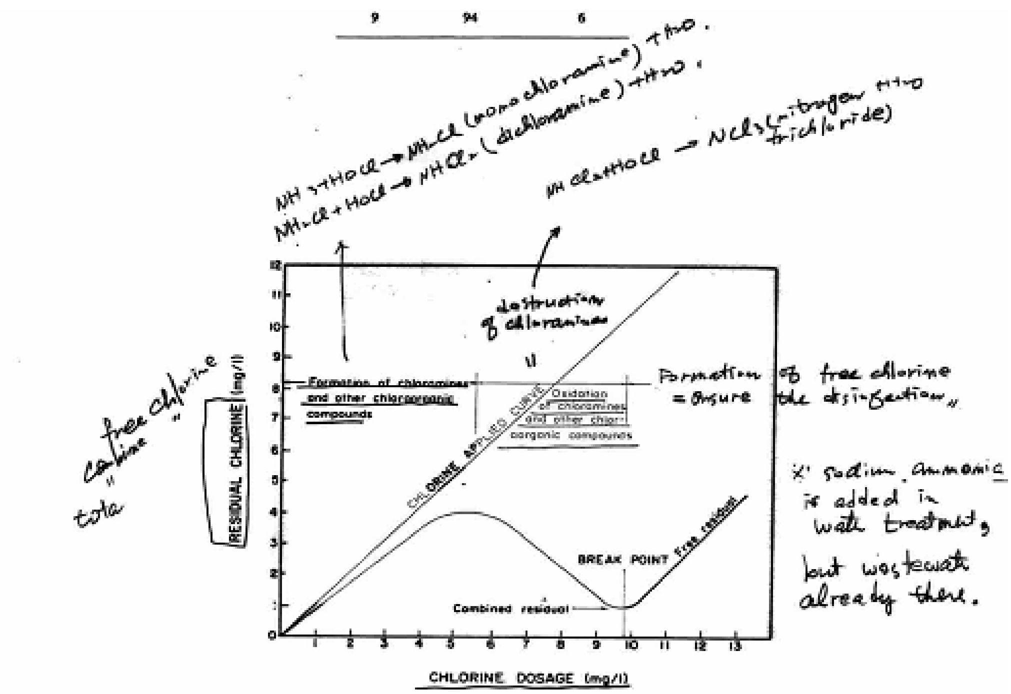


Figure 14.1. Residual chlorine curve showing break point.

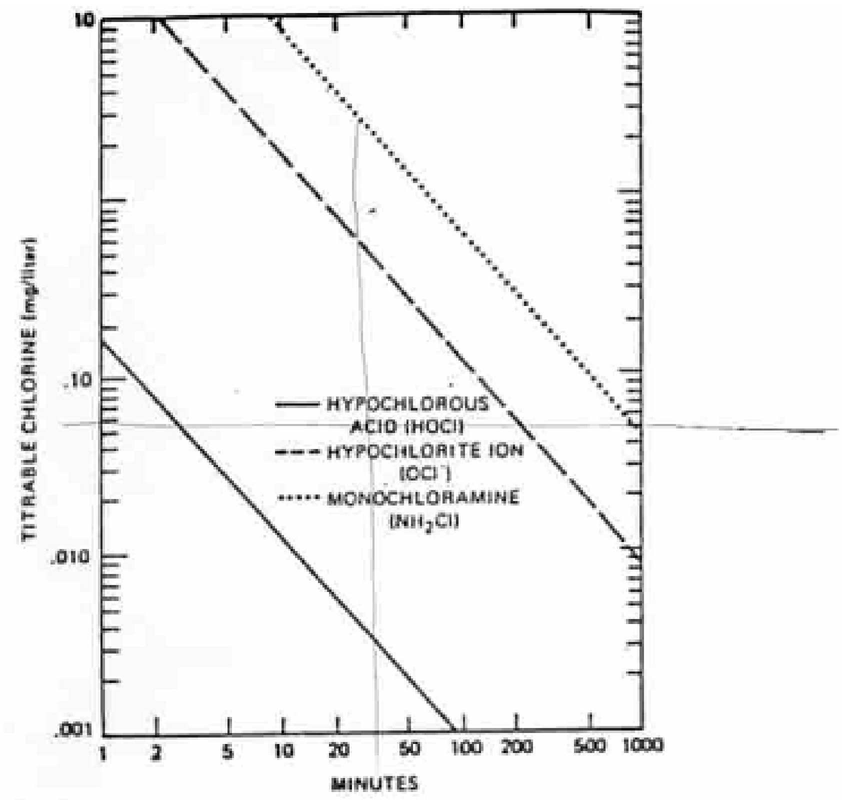


Figure 1. Concentration vs Time for 99 % Inactivation of E. Coli.

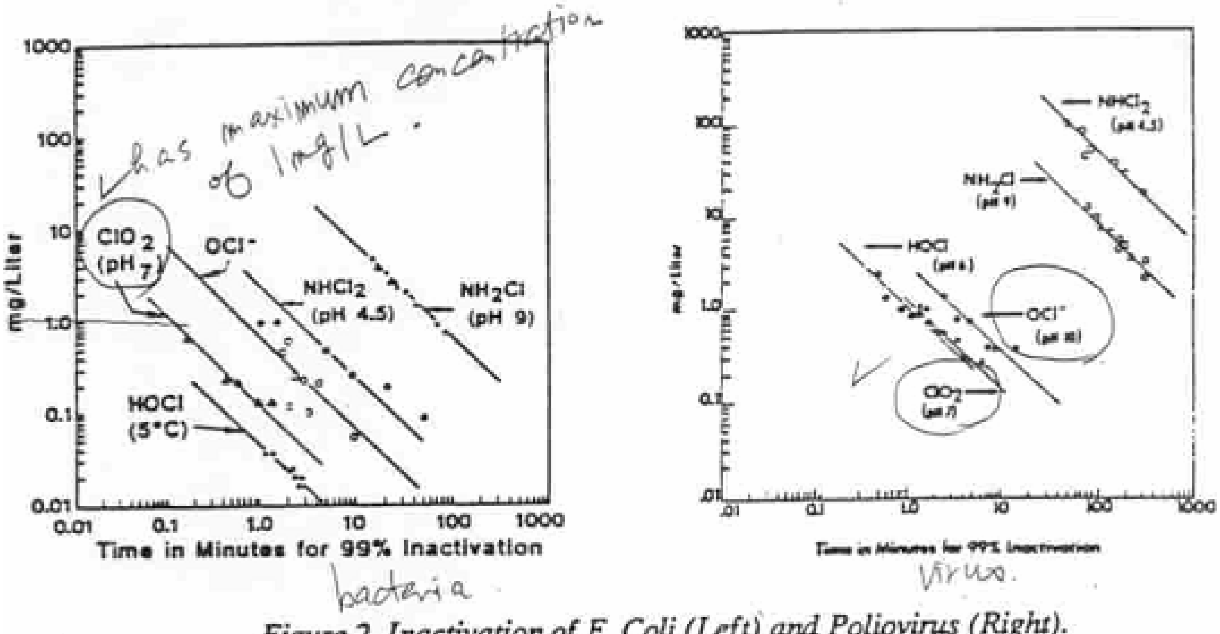


Figure 2. Inactivation of E. Coli (Left) and Poliovirus (Right).

■ Proposed New Rules:

- New, more restrictive for THM, HAA, Bromate
- Required disinfection of groundwater
- C-T values (mg/L)(min.)
    - Based on Giardia (3-log reduction, 99.9%) ad virus (4-log) inactivation
    - only @ plants, not value out of plant

■ C-T values

- C-T values represent concentration-time relationships that embody disinfection requirements.
- Disinfection treatment requirement is part of SWT Rule.
- C-T values are specified as a function of pH and temperature.
- Protection is measured by log inactivation of Giardia cysts and enteric viruses.
- Pre-disinfection/pre-oxidant credit is allowed if the raw water turbidity is < 5 NTU for Giardia or < 1 NTU for viruses C-T requirements. This stipulation could cause havoc with utilities contemplating O_3 + NH_2Cl !
- For ozone, there is a problem associated with the instability and short half-life ($t_{1/2}$ = 20min.). The question arises: what concentration must be specified in the C-T relationship? EPA states that the calculation should be based on ozone residual (mg/L) in the effluent multiplied by the hydraulic residence time (min) of the contact basin. If several sequential ozone contactors are used, the calculation of the overall C-T value may be taken as the sum of each individual C-T value from each compartment (tracer studies can be used to define contact time of each compartment).

Table 1. Values for 99.9% inactivation of Giardia Lamblia.

		Temperature (℃)					
	pH	0.5	5	10	15	20	25
Free chlorine (2mg/L)	6	170	120	90	60	46	30
	7	260	190	130	100	70	47
	8	380	270	190	140	101	67
	9	520	370	260	190	139	93
Ozone	6-9	5	3	2.5	2	1.5	1.0
Chlorine dioxide	6-9	81	54	40	27	21	14
Chloramines (preformed)	6-9	3,300	2,300	1,700	1,100	850	550

Table 2. CT values for ozone inactivation of Giardia (pH = 6-9).

Removal	Temperature (℃)					
	0.5	5	10	15	20	25
0.5 log	0.8	0.5	0.4	0.4	0.3	0.2
1.0 log	1.7	1	0.8	0.7	0.5	0.3
1.5 log	2.3	1.5	1.3	1.0	0.8	0.5
2.0 log	3.3	2.0	1.7	1.3	1.0	0.7
2.5 log	3.7	2.5	2.1	1.7	1.2	0.8
3.0 log	4.5	3.0	2.5	2.0	1.5	1.0

Table 3. Proposed CT requirements for ozone inactivation of Cryptosporidium parvum oocysts.

Inactivation ($-\log_{10}(N/N_0)$)	CT (mg-min./L)						
	@0.5℃	@5℃	@10℃	@15℃	@20℃	@25℃	@30℃
0.5	20.1	11.3	6.08	3.34	1.87	1.07	0.62
1.0	32.7	18.4	9.88	5.43	3.05	1.74	1.01
1.5	45.3	25.4	13.7	7.52	4.22	2.41	1.40
2.0	57.9	32.5	17.5	9.60	5.39	3.08	1.79
2.5	70.4	39.5	21.3	11.7	6.56	3.75	2.18
3.0	83.0	46.6	25.1	13.8	7.73	4.42	2.57
3.5	95.6	53.7	28.9	15.9	8.90	5.09	2.96
4.0	108	60.7	32.7	18.0	10.1	5.76	3.35
4.5	121	67.8	36.5	20.0	11.2	6.43	3.74
5.0	133	74.8	40.3	22.1	12.4	7.10	4.13
5.5	146	81.9	44.0	24.2	13.6	7.77	4.52
6.0	158	88.9	47.8	26.3	14.8	8.44	4.91

■ Distribution system regrowth

- Ozone oxidizes complex, "biorefractory" humic and fulvic acid molecules to partial oxidation by-products that are more "bioavailable". This transformation involves the creating of lower molecular weight by-products from higher molecular weight humic substances. Due to their smaller molecular size as well as other molecular-structure changes, these by-products are more biodegradable. Problems of regrowth arise when biodegradable organic matter is introduced into a water distribution system. Regrowth can lead to taste and odor (T & O) problems while also creating conditions conducive to the proliferation of bacteria in general (as reflected by heterotrophic plate counts, HPC) as well as coliform bacteria in specific (as reflected by total coliform assays, TC).
- "Regrowth" or "aftergrowth" refers the multiplication of bacteria in a distribution system after treatment. A major factor influencing the extent of bacterial regrowth in drinking water is the presence of organic and inorganic compounds which serve as energy sources for bacteria. Regrowth potential is ascertained by measuring AOC, assimilable organic carbon, along with dissolved organic carbon, DOC.
- Measurements of AOC: The measurement of AOC is based on determining the maximum growth rate of a selected bacterium (e.g., Psudomonas fluoresceins). The original bacteria from the sample are eliminated by heating. From the maximum level of growth (maximum colony count), the concentration of AOC originally available to the selected bacterium is calculated by using its yield value for a selected known substrate (e.g., acetate). Thus, the AOC concentration is expressed as the concentration of organic carbon in the selected known substrate giving a maximum colony count similar to the colony count observed for the "unknown". AOC results are often reported in terms of [μg of acetate C equivalents per liter]. Corresponding DOC measurements are also reported. Typical AOC levels in untreated river water (DOC;

3-4 mg/L) are 10 to 50 μg/L, while ozonated waters can exhibit levels in excess of 100 μg/L.

- Implications: The ratio of AOC/DOC is a direct indication of the bioavailability of the DOM present in a water. In ascertaining treatment effects on AOC, it is important to recognize that some water treatment processes removal DOM molecules "intact" (e.g., adsorption, coagulation) while other processes (e.g., ozonation) merely transform the DOM into simpler (and presumably more bioavailable) forms.
- River water generally contains less than 100 μg/L of AOC, while AOC concentration of less than 10 μg/L have been reported in groundwater. Chemical coagulation causes a significant (50-90%) reduction in AOC. Granular activated carbon (GAC) adsorption also generally decreases AOC, although ozonation preceding GAC columns has yielded mixed trends. Chlorination can induce a small increase in the overall biodegradability of organics in water.
  - Ozonation is normally accompanied by an increase in AOC concentration with little overall effect on DOC levels. It has been suggested that the production of carboxylic acids by ozone is largely responsible for this trend. Some results from the Netherlands are presented:
  -

Sample	DOC (mg/L)	AOC (μg/L)	AOC/DOC (μg/mg)
Before O_3	7.2	15	2.1
After O_3	7.1	120	16.9
Before O_3	4.0	33	8.3
After O_3	3.8	105	27.6
Before O_3	3.0	12	4.0
After O_3	2.9	91	31.4

■ Distribution system nitrification

- Nitrification has been observed in the distribution systems of water utilities that have changed their disinfection practice from free chlorine to chloramination. Chloramination, predicted on the formation of monochloramine, is based on the following stoichiometry:

$HOCl + NH_3$ ---> $NH_2Cl + H_2O$

- The stoichiometric ration of chlorine to ammonia is 1:1, reflecting a weight ration of 4.2:1 for (HOCl as Cl_2):NH_3 or 5.1:1 for (HOCl as Cl_2):(NH_3 as N). A key concern is the ratio of ammonia nitrogen, NH_3-N, to chlorine, Cl_2, that is maintained at a water utility.
- If the ratio (chlorine to ammonia) is less than the indicated stoichiometric relationship, free ammonia will exist. If greater, some dichloramine, $NHCl_2$, can be formed, depending on pH conditions. Once in the distribution system, monochloramine can slowly decompose or hydrolyze, providing a source of ammonia:

$NH_2Cl + H_2O$ --> $NH_3 + HOCl$

- Others have found a buildup of nitrite, NO_2^-, in storage reservoirs receiving chloraminated water. It was ascertained that excess ammonia was being oxidized to NO_2^- by ammonia oxidizing bacteria (e.g., Nitrosomonas), but that water quality conditions were inhibitory to nitrite oxidizing bacteria (e.g., Nitrobacter). It is important to recognize that nitrite exerts a significant chlorine demand, with nitrite reacting more readily with free chlorine than does ammonia. Recent evidence suggests that nitrite may directly react with monochloramine. Others have found that development of a significant nitrifier population can potentially stimulate the growth of other bacteria by releasing assimilable organic compounds.

■ Other distribution system concerns: Proposed Lead Rule

- MCL = 10 μg/L
- Corrosion control:
    - pH > 8.0
    - Alkalinity > 30 mg/L as $CaCO_3$
- Water conditioning : Adjust pH, alkalinity, and calcium to make water slight encrustive (i.e., slight ability to precipitate a protective coating of $CaCO_3$) in distribution system.

■ CONDITIONING (Chemical conditioning/stabilization)

- Adjustment of pH, Ca^{2+}, and alkalinity of water to saturation/equilibrium (slightly saturation)
- Conditioning chemicals :
    1) to lower pH :
    2) to raise pH :

Encrustive (Supersaturated) versus Aggressive (Corrosive; Undersaturated)

-

, here,

please recall,

- Comparing equilibrium pH_{eq} and pH actually measured ⇒ LI (Langlier Index)=pH_m - pH_{eq}

when LI = 0, equilibrium

LI > 0, supersaturated, i.e., encrustive

LI < 0, undersaturated, i.e., aggressive

Example: Compute LI for the following water:

pH=7.55, Ca^{2+}=150mg/L as $CaCO_3$, HCO_{3-} alkalinity=160mg/L as $CaCO_3$.

Given information: pK_s=8.15, pK_2=10.49, K_s=7.9x10^{-9}, K_2=3.24x10^{-11}

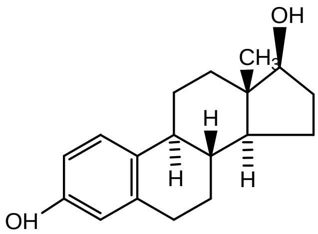
(Solutions)

Lecture 2: Engineering Mathematics and Fundamental Transport Phenomena

- Scalars, vectors and tensors
- Kinematics
- Equations of continuity
- Linear momentum principle
- Cauchy’s equation of motion
- Navier-Stokes equation
- Order-of-magnitude analysis of Navier-Stokes equation
- Creeping flow equation
- Brief introduction of solutions of the creeping flow equation

Lecture 3: Introduction to Membrane Technology

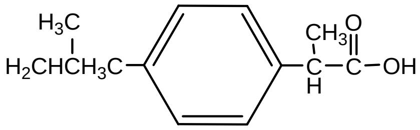
Why membranes?



>90% by Cl_2

>90% by O_3

17β-Estradiol



10~20% by Cl_2

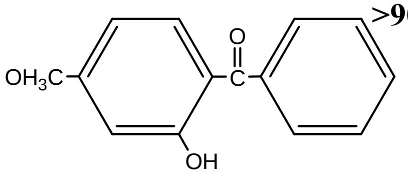
56-95% by O_3

Ibuprofen

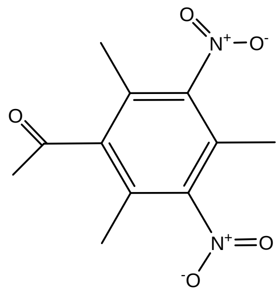
>90% by Cl_2

>90% by O_3

>90% by PAC



Oxybenzone(sunscreen)

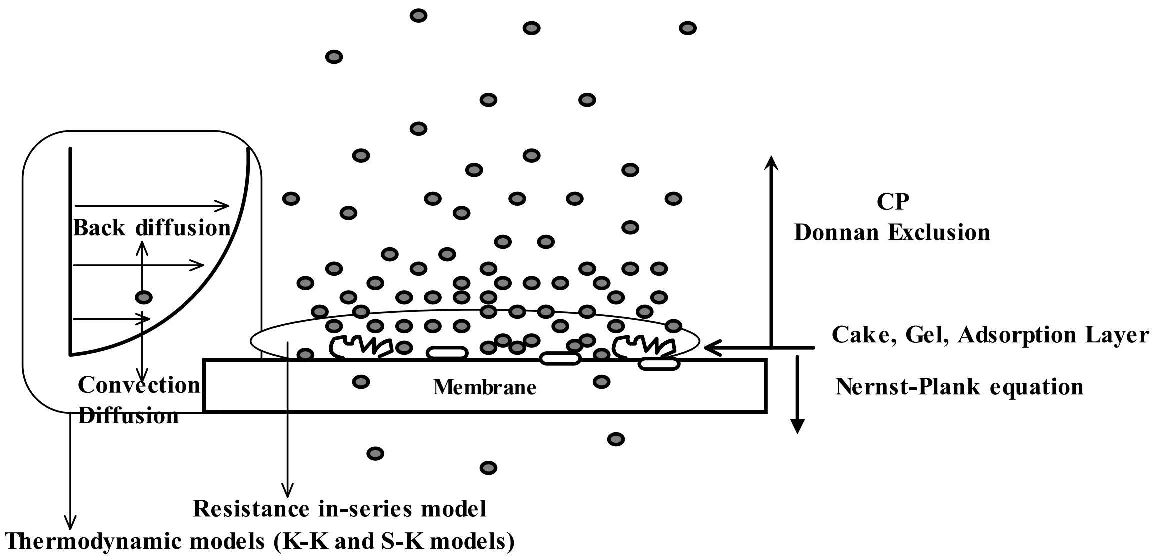


~25% by Cl_2

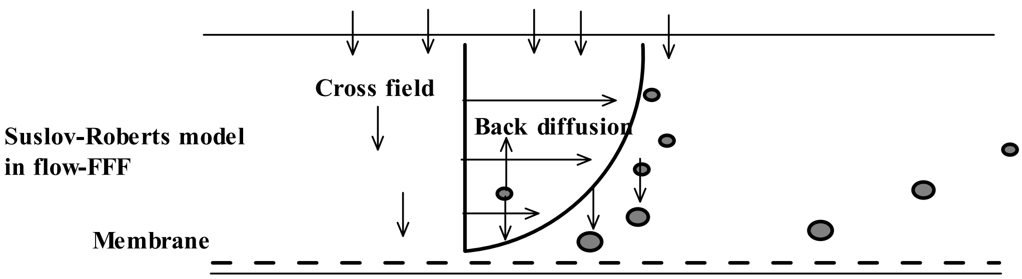
~30% by O_3

~70% by PAC

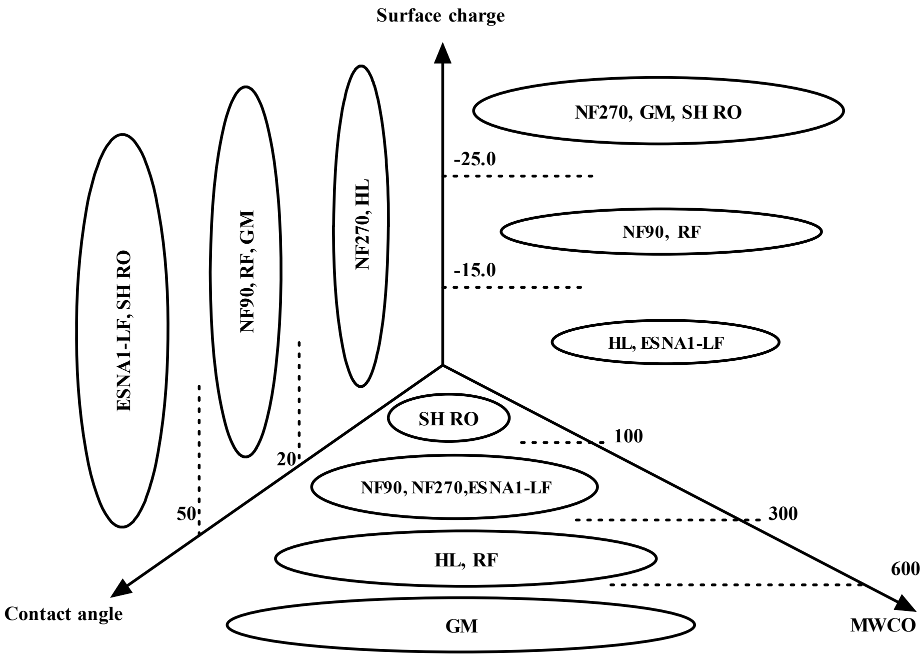
Musk ketone



Back diffusion
Convection
Diffusion
Membrane
CP
Donnan Exclusion
Cake, Gel, Adsorption Layer
Nernst-Plank equation
Resistance in-series model
Thermodynamic models (K-K and S-K models)



Cross field
Back diffusion
Suslov-Roberts model
in flow-FFF
Membrane



Surface charge
NF270, GM, SH RO
-25.0
NF90, RF
-15.0
HL, ESNA1-LF
ESNA1-LF, SH RO
NF90, RF, GM
NF270, HL
SH RO
100
NF90, NF270,ESNA1-LF
300
HL, RF
600
GM
20
50
Contact angle
MWCO

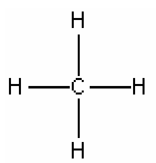
Lecture 4: Introduction to Organic Chemistry

* Organic chemistry is chemistry of carbon and carbon compounds
* Carbon atom:
  - Four electrons in valence shell:
  - Strives for eight to reach a stable configuration
  - Carbon can readily form covalent bonds
  - A striking properties
    - can share electrons with atoms of their own kind to form a long chain
  - Various elements can form covalent bonds with carbon
    H, O, N, Halogens (Cl, Br, etc.)
  - Carbon can assume several oxidation states, permitting it to form covalent bonds with various elements (-4 to +4)

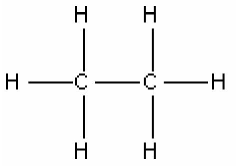
* Classes of organic compounds
  Saturated Hydrocarbons
  Unsaturated Hydrocarbons
  Aromatic Hydrocarbons
  Alcohols and Phenols
  Aldehydes and Ketones
  Carboxylic Acids
  Fats and Oils
  Amines
  Carbohydrates
  Amino Acids and Proteins

* Hydrocarbons (CaHb)
  - General Observations
    - Most hydrocarbons are soluble in water
    - Most hydrocarbons are relatively toxic to aqueous organisms and humans
    - Some hydrocarbons are resistant to biodegradation

* Saturated Hydrocarbons (Alkanes): Only single bonds are present; General formula C_nH_{2n+2}
  By International Union of Pure and Applied Chemistry (IUPAC)



CH_4 methane (gas)

 C_2H_6 ethane (gas)

C_3H_8 propane

C_4H_{10} butane

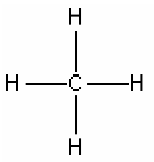
C_5H_{12} pentane

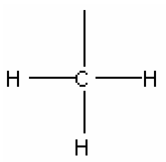
C_6H_{14} hexane Liquids at STP

C_7H_{16} heptane

C_8H_{18} octane

- Naming substitution groups (i.e., replace H)
  - Alkyl group ... derived from alkanes by removing one H.



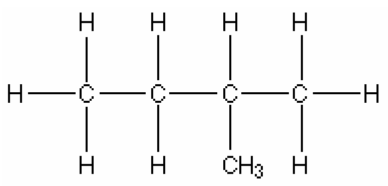
 ($-CH_3$) Methyl group

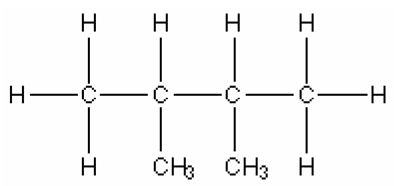
  - Halogen groups

  Chloro = Cl, Fluoro = Fl, Bromo = Br, Iodo = I

  - Nitro groups: NO_2

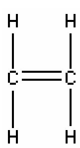
- Naming hydrocarbons with substitution groups

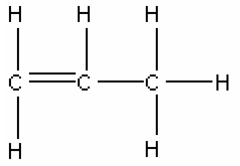
 methyl butane

 2,3 dimethyl butane

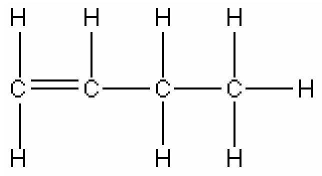
* Unsaturated Hydrocarbons (Alkenes)

- Hydrocarbons that has a double bond
- Alkenes have general formula C_nH_{2n}

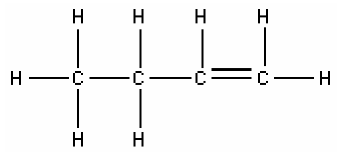
 ethene (commonly, ethylene)



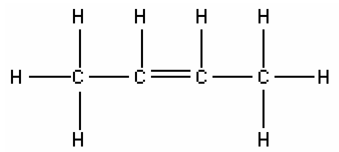
propene



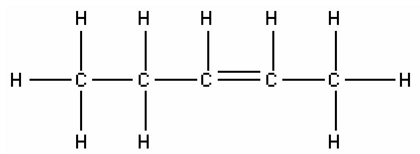
1-butene (1- refers to locations of double bond)



1-butene

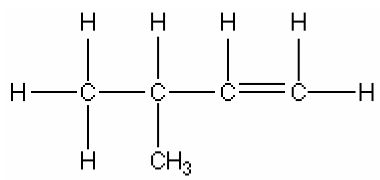


2-butene



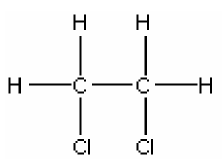
2- pentene

- Alkenes with 4 or less carbons ... Gases; water solubility $\propto$ 1/MW
- Naming hydrocarbons with substitution groups
  - Similar to Alkanes
  - Always base numbers on location of double bond



3 methyl 1-butene

- Reactions of Alkenes
  - (1) Addition reactions (i.e., addition to double bond)

CH_2=CH_2 + Cl_2 $\rightarrow$  1,2 dichloroethane (toxic)

(2) Chemical oxidation reactions

(3) Substitution reaction

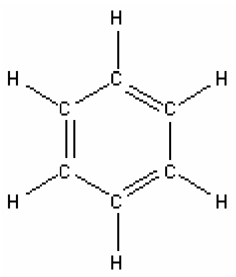
(4) Biological oxidation

(5) Polymerization

$n\ CH_2{=}CH_2 \rightarrow (C_2H_4)_n$, n=70~700 (at high T and pressure)

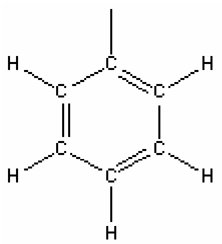
* Aromatic Hydrocarbons

- Most simple aromatic hydrocarbon

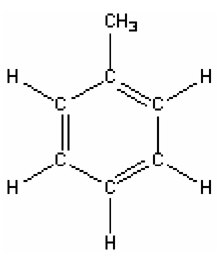


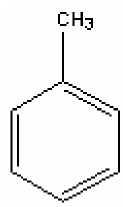
Benzene

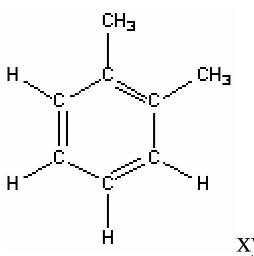
- Most simple aromatic radical (substituent)

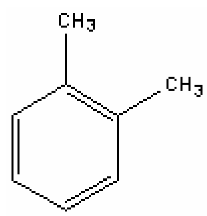


benzyl group

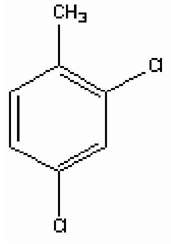
- 

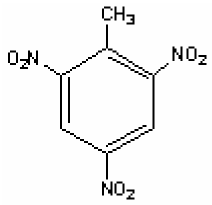
toluene (methyl benzene by IUPAC) 

- 

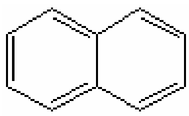
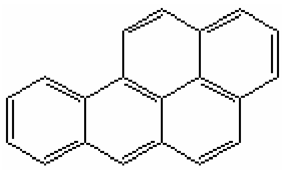
xylene (dimethyl benzene by IUPAC) 

- More complicated aromatics with substitution groups

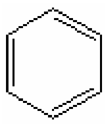
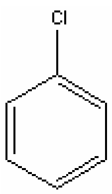
 2,4 dichlorotoluene

 2,4,6 trinitrotoluene (TNT)

- Polynuclear aromatic hydrocarbons
  - Two or more benzene rings

 naphthalene  benzopyrene

- Reactions:
  (1) Substitution reactions:

 + Cl_2 →  chlorobenzene (benzyl chloride)

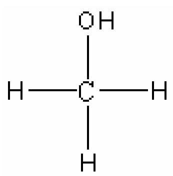
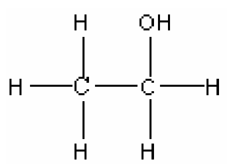
(2) Chemical oxidation rxns:
- Side chains are readily oxidized
- Aromatic rings rather resistant to oxidation (a limitation of COD test)

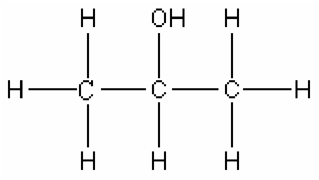
(3) Biological oxidation ... certain strains can break ring

* Alcohols and Phenols

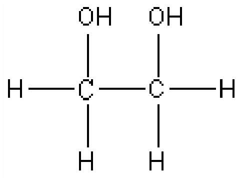
Alcohols = similar to Alkane/Alkenes except H replaced by OH
Phenols = similar to Aromatic Hydrocarbons except H replaced by OH

(Alcohols)

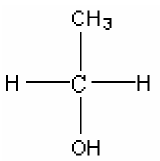
 methanol (methyl alcohol)  ethanol (ethyl alcohol)

 2 propanol (2 refers to location of OH group)

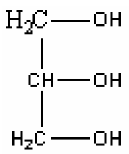
- Two OH groups:

 ethandiol

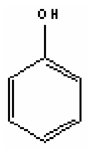
- Substitution groups:
  - Named in similar systematic fashion:

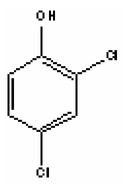
 2-methyl 2-propanol

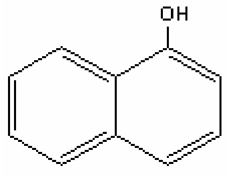
- Glycerols:
  - A special type of Alcohols
  - includes three OH groups

 propantriol (glycerol)

  - Fats have a glycerol-type structure
    - Glycerols related to structure of fats (glycerides)
- Phenols
  - Most simple phenol



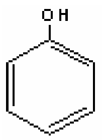
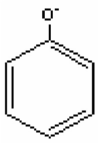
    - Substitution groups:  2,4 dichlorophenol
  - Multi-ring phenols (polyphenols)


1-naphthol

- Solubility of Alcohols and Phenols in Water
  - Alcohols: solubility decreases with increasing chain length
  - Phenols: simple phenol is moderately soluble in cold water; much ring less soluble

- Acidity of Alcohols and Phenols
  - Both Alcohols and Phenols behave as acids (i.e., proton donors); Alcohols are weaker acids than water (considered virtually non-ionized)
  - Phenol is a stronger acids than water (weak acids nevertheless)

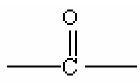
  ROH ⇔ $RO^- + H^+$, $K_a=10^{-20}$ (ionization constant)

 ⇔  + H^+, $K_a=10^{-10}$ (cf. $K_w = 10^{-14}$)

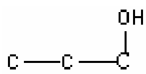
- Rxns of Alcohols and Phenols
  (1) Chemical oxidation
  - Most alcohols readily susceptible to oxidation
    eg, ethanol in wine → acetic acid (vinegar) in air (O_2)
  - Phenols are much more resistant to oxidation

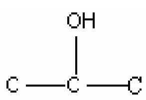
  (2) Substitution/Halogenation

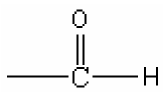
* Aldehydes and Ketones

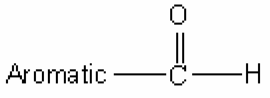
- Both contain carbonyl group 

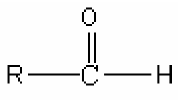
cf. Aldehydes: oxidation products of primary alcohols (OH attached to terminal (single) carbon)



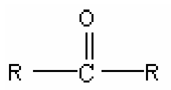
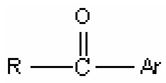
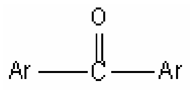
Ketones: oxidation products of secondary alcohols (OH attached to carbon atom joined with two other carbons) 

- If one of two groups attached to carbonyl group is an H, compounds are Aldehydes 

(examples)  Aromatic Aldehydes

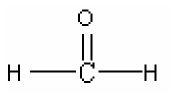
 Aliphatic Aldehyde (R=alkyl group)

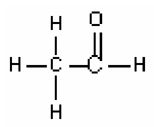
- If neither of two groups attached to carbonyl group is an H, compound are Ketones

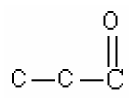
  

aliphatic ketone mixed ketone aromatic ketone

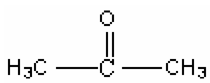
- Nomenclature
  1) Aldehydes

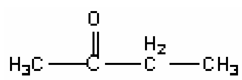
 Formaldehyde (methanal by IUPAC)

 Acetadehyde (ethanal)

 Propionaldehyde (propanal)

  2) Ketones

 Acetone (propanone)

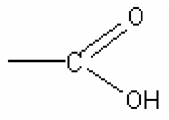
 Methyl Ethyl Ketone (2-butanone)

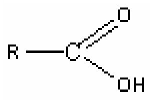
- Reactions
  (1) Oxidation
  - Aldehydes are easily oxidized
  - Ketones are only oxidized when severe condition

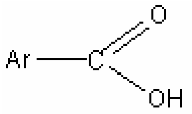
  (2) Addition to double bond: fairly rare

  (3) Substitution

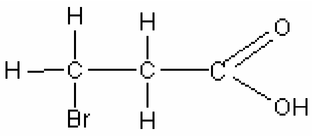
* Carboxylic Acids
  - Most important class of organic acids; represents highest oxidation state that C can attain
  - contains the carboxyl group



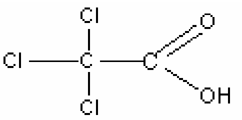
 or RCOOH Aliphatic carboxylic group

 or ArCOOH Aromatic carboxylic group

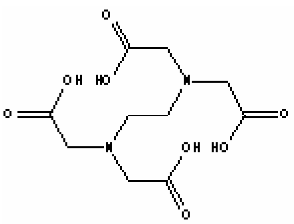
- consider Aliphatic carboxylic acid; also called Fatty acids (many were first isolated from natural fats)
- Substitution groups
    - numbered from the carboxylic carbon to substituent position:

 3-bromopropanoic acid

- Acidity of carboxylic acids
    - Most carboxylic acids have a K_A of about 10^{-5}
    - Most qualify as week acids with a few exceptions
        - Exceptions:

 $K_{eq} = 2\times10^{-1}$

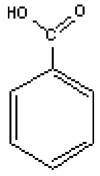
- Polycarboxylic acids
    - consider EDTA (ethylene diamine tetra-acetic acids); four carboxylic groups



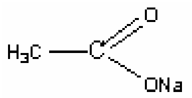
R	Common name	IUPAC name
HCOOH	formic acid	mathanoic acid
CH_3COOH	acetic acid	ethanoic acid
CH_3CH_2COOH	propionic acid	

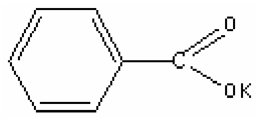
- Above are known as volatile fatty acids; important in anaerobic digestion of sewage sludge
- Under anaerobic conditions: Sludge Organics→Volatile Fatty Acids→CH_4+CO_2
  acid forming bacteria methane forming bacteria

- Aromatic carboxylic acids:

 Benzoic acid

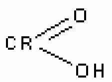
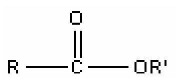
- can employ carboxylic acids and their salts in buffer solution:
  (ex.) HAc and NaAc
  , taking log;
  thus,
- Salts of carboxylic groups
  - Carboxylic acids react with bases to form salts
    HAc + NaOH → NaAc + H_2O
  - Salts of organic acids are named like salts of inorganic acids

 sodium acetate

 potassium benzoate

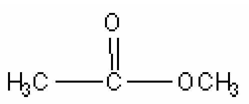
  - Sodium and Potassium salts of long chain Fatty Acids = Soaps
    $RCOO^-Na^+$ ($R=C_{15}$)
  - Salts of Fatty Acids vary in solubility (solubility ∝ 1/MW)
- Solubility of Carboxylic Acids:
  - Lower molecular weight aliphatic acids (i.e., Fatty Acids) are significantly soluble in water
  - Unionized forms are less soluble

* Esters
- Related to both Acids and Alcohols
- Products of Acids and Alcohols
- Produced during following reactions

 + R'OH →  : this occurs only under certain conditions

acid alcohol ester (characteristic group = COO)

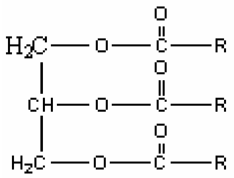
- Named in a manner similar to salts of weak acids

 Methyl acetate

- Fats are esters
  - Also have a glycerol (three OH group)

* Fats and Oils

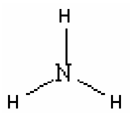
- Naturally occurring groups of organic materials known as lipids
- Constituents of plants and animals: insoluble in water
- Fats and Oils are differentiated by their differences in melting points:
  Fats are solids at room temperature, and Oils are liquids at room temperature
- Fats and Oils are Esters of Glycerols (a triol) (i.e., a glyceride)
- Consider a generated Glyceride



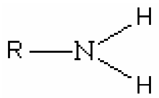
- Fats represent one of the basic food stuffs ... Metabolic sources of energy
- Fats also represent an important component of the organic fraction of sewage/wastewater

* Amines

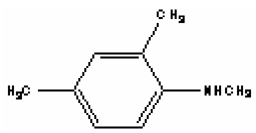
- Organic Bases
- Amines bear a strong resemblance to ammonia



- Classification depends on whether one, two, or three hydrogen atoms of ammonia have been replaced with organic groups



Primary Amine

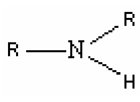


N-methyl 2,4 dimethyl aniline

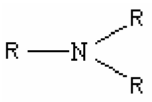
- General characterizations of Amines
  - Lower members (low MW) are gases with are readily soluble in water (like NH_3)
  - Amines behave as weak bases in water
  - Consider a primary amine

  $RNH_2 + H_2O \leftrightarrow RNH_3^+ + OH^-$

  - In general, aliphatic amines are slightly stronger bases than ammonia



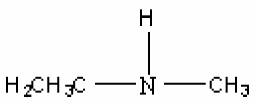
Secondary Amine

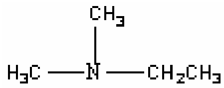


Tertiary Amine

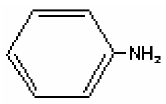
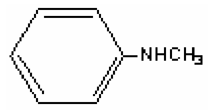
  - examples:

  CH_3NH_2 methyl amine

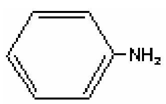
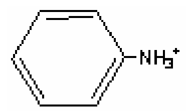
 methyl ethylamine

 dimethyl ethylamine

- Aromatic Amines: Most simple aromatic amine

 aniline,  N-methylaniline, Here N indicates substituent group is attached to nitrogen

- In constrast, aromatic amines are much weaker bases

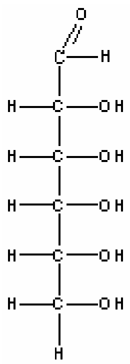
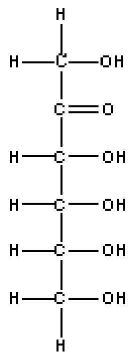
 + H_2O ↔  + OH^- : $K_b=4.2\times10^{-10}$ (i.e., pH=4.6)

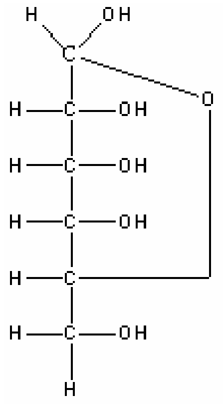
Please refer to $K_b=2\times10^{-5}$ (i.e., pH=9.3)

* Carbohydrates

- An important class of naturally occurring compounds; includes sugars, starches, and celluloses
- Structurally, carbohydrates are polyhydroxy aldehydes or polyhydroxy ketones
- Carbohydrates are classified according to Monosaccharides, Oligosaccharides, Polysaccharides (here mono=one, oligo=few, poly=many)
- Monosaccharides are simplest carbohydrates:

  Example: Glucose (polyhydroxy aldehyde), Fructose (polyhydroxy ketone)

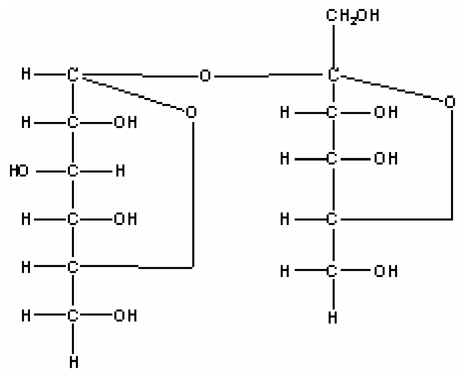
 Glucose ($C_6H_{12}O_6$)  Fructose ($C_6H_{12}O_6$)



cyclic forms of Glucose

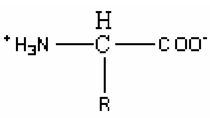
- Cyclic structure is important in linking monosaccharide units into oligo and polysaccharides
- Basic building blocks: cyclic forms of monosaccharides

* Disaccharides
  - Comprised of two monosaccharides
  - Sucrose is the most important ($C_{12}H_{22}O_{11}$)

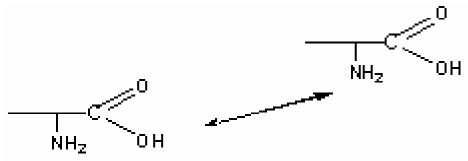


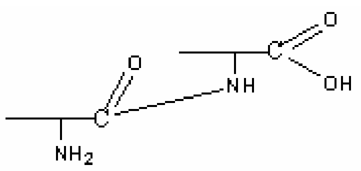
cyclic glucose   cyclic fructose

* Polysaccharides
  - comprised of many mono-saccharide units
  - cellulose and starch are examples

* Amino Acids and Proteins
  - Proteins
    - Polymers comprised of amino acid units joined by amide linkage
    - present in all living matters
    - 27 α Amino Acids have been identified as building blocks of protein
    - Proteins contain various numbers of α amino acids: 

    - Properties of proteins determined by amino acid make-up





Amide Link; also called polypeptides (base-acid = peptide link)