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CEE 370 Environmental Engineering Principles

Lecture #8

Environmental Chemistry VI: Acids-bases III, Organic Nomenclature

Reading: Mihelcic & Zimmerman, Chapter 3

Davis & Masten, Chapter 2
Mihelcic, Chapt 3

Steps in Solving chemical equilibria

1. List all chemical species or elemental groupings that are likely to exist
   - Cations: Na^{+}, K^{+}, Ca^{+2}, NH_4^{+}, H^{+}, etc.
   - Anions: NO_3^{-}, Cl^{-}, SO_4^{-2}, OH^{-}, PO_4^{-3}, HPO_4^{-2}, $H_2PO_4^{-}$, Ac^{-}, HCO_3^{-}, CO_3^{-2}, etc.
   - Neutral species: NH_3, HAc, H_3PO_4, H_2CO_3, etc.
   - note that ionic salts (e.g., NaCl, KCl) completely dissociate in water an thus should not be listed.

Steps in Solving chemical equilibria (cont)

2. List all independent chemical equations that involve the species present, including:

A. Chemical Equilibria
   - E.g., acid base equilibria

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 10^{-6.3}$$

$$K_2 = \frac{[H^+][CO_3^{-2}]}{[HCO_3^-]} = 10^{-10.3}$$

B. Mass Balance equations
   - Total amount of each element is conserved

$$C_{carbonates} = [H_2CO_3] + [HCO_3^-] + [CO_3^{-2}] = 10^{-3}$$ and $$C_{sodium} = [Na^+] = 10^{-3}$$

C. Electroneutrality or charge balance
   - All water solutions must be neutrally charged

$$[H^+] + [Na^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{-2}]$$

Steps in Solving chemical equilibria (cont)

3. Solve the equations
   - You should have as many independent equations as chemical species
   - Often it is easiest to solve for H^+ and then use that concentration to calculate all other species

Example 4.11

Determine the species present if the following compounds are dissolved into water, in both open and closed systems:

a) Sodium carbonate, [Na_2CO_3]
b) Sodium bicarbonate, [$NaHCO_3$]
c) Sodium phosphate, [Na_3PO_4]

Solution to 4.11 a)

First the sodium carbonate will dissolve

$$Na_2CO_3(s) \rightarrow 2\,Na^{2+} + CO_3^{2-}$$

Then the carbonate can become protonated

$$H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$$

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3(aq)$$

$$H_2CO_3(aq) \leftrightarrow H_2O + CO_2(aq)$$

Finally, in an open system, the carbon dioxide can escape as a gas

$$CO_2(aq) \leftrightarrow CO_2(g)$$

Solution to 4.11 b)

First the sodium bicarbonate will dissolve

$$NaHCO_3(s) \rightarrow Na^+ + HCO_3^-$$

Then the bicarbonate can become protonated or deprotonated

$$H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$$

$$H^+ + HCO_3^- \leftrightarrow H_2CO_3(aq)$$

$$H_2CO_3(aq) \leftrightarrow H_2O + CO_2(aq)$$

Finally, in an open system, the carbon dioxide can escape as a gas

$$CO_2(aq) \leftrightarrow CO_2(g)$$

Solution to 4.11 c)

First the sodium phosphate will dissolve

$$Na_3PO_4 \rightarrow 3Na^+ + PO_4^{3-}$$

Then the phosphate can become protonated

$$H^+ + PO_4^{3-} \leftrightarrow HPO_4^{2-}$$

$$H^+ + HPO_4^{2-} \leftrightarrow H_2PO_4^-$$

$$H^+ + H_2PO_4^- \leftrightarrow H_3PO_4(aq)$$

Finally, in an open system, there are no additional species to consider, because there are no gas-phase forms of phosphate

Carbon Forms: Definitions

Inorganic Carbon (+IV oxidation state)

CO_2 = carbon dioxide (dissolved and gas)
H_2CO_3 = carbonic acid (dissolved)
HCO_3^- = bicarbonate (dissolved)
CO_3^{-2} = carbonate (dissolved)
$CaCO_3$ = calcium carbonate (mineral)

Organic Carbon (< +IV oxidation state)

$C_6H_{12}O_6$ = glucose (a sugar)
CH_3COOH = acetic acid (a carboxylic acid)

The Carbonate System

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3$$

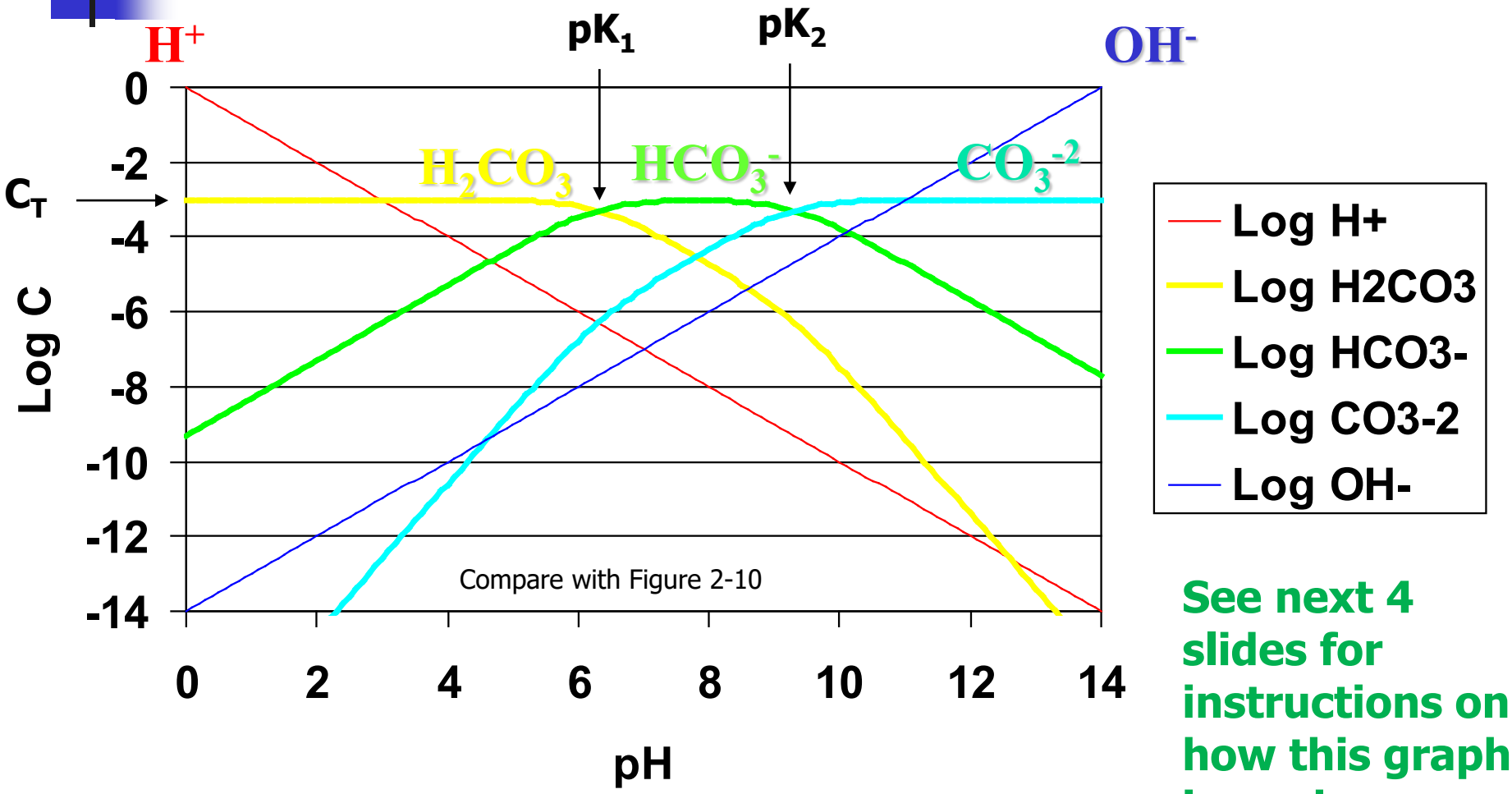
- Major buffer ions
- volatile: interaction with atmosphere
- biologically active

- Definitions:

$$[CO_2(aq)] + [H_2CO_3] = [H_2CO_3^*]$$

$$[H_2CO_3^*] + [HCO_3^-] + [CO_3^{-2}] = C_T$$

Carbonate System ($C_T=10^{-3}$)



See next 4 slides for instructions on how this graph is made

Rapid Method for Log C vs. pH Graph

- 1. Plot diagonal $[H^+]$ and $[OH^-]$ lines
- 2. Draw a light horizontal line corresponding to log C_T
- 3. Locate System Point
  - i.e., pH = pK_a, log C = log C_T
  - make a mark 0.3 units below system point
- 4. Draw 45º lines (slope = ± 1) below log C_T line, and aimed at system point
- 5. Approximate curved sections of species lines ± 1 pH unit around system point
- 6. Repeat steps as necessary for more complex graphs
  - #3-#5 for additional pK_as of polyprotic acids
  - #2-#5 for other acid/base pairs

Diprotic acids: calculations

- Start with C_T and K_a equations

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]}$$

$$K_2 = \frac{[H^+][A^{-2}]}{[HA^-]}$$

$$C_T = [H_2A] + [HA^-] + [A^{-2}]$$

$$[HA^-] = \frac{K_1[H_2A]}{[H^+]}$$

$$[A^{-2}] = \frac{K_2[HA^-]}{[H^+]} = \frac{K_1K_2[H_2A]}{[H^+]^2}$$

$$C_T = [H_2A] + \frac{K_1[H_2A]}{[H^+]} + \frac{K_1K_2[H_2A]}{[H^+]^2}$$

$$C_T = [H_2A]\left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right)$$

$$\frac{[H_2A]}{C_T} = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}}$$

Diprotic acids: calculations (cont.)

- Use $[H_2A]/C_T$ and K_a equations to get other α's

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]} \rightarrow \frac{K_1}{[H^+]} = \frac{[HA^-]}{[H_2A]} \qquad \frac{K_2}{[H^+]} = \frac{[A^{-2}]}{[HA^-]} \leftarrow K_2 = \frac{[H^+][A^{-2}]}{[HA^-]}$$

For distribution diagrams

$$\frac{[H_2A]}{C_T} = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}}$$

α_0

$$\frac{[HA^-]}{C_T} = \frac{[H_2A]}{C_T}\frac{[HA^-]}{[H_2A]} = \frac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}}\left(\frac{K_1}{[H^+]}\right)$$

$$\frac{[HA^-]}{C_T} = \frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}}$$

α_1

$$\frac{[A^{-2}]}{C_T} = \frac{[HA^-]}{C_T}\frac{[A^{-2}]}{[HA^-]} = \frac{1}{\frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}}\left(\frac{K_2}{[H^+]}\right)$$

$$\frac{[A^{-2}]}{C_T} = \frac{1}{\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1}$$

α_2

Note: $\alpha_0 + \alpha_1 + \alpha_2 = 1$

Diprotic acids: calculations (cont.)

$$\alpha_0 \equiv \frac{[H_2A]}{C_T} \qquad \alpha_1 \equiv \frac{[HA^-]}{C_T} \qquad \alpha_2 \equiv \frac{[A^{-2}]}{C_T}$$

$$\frac{1}{1+\frac{K_1}{[H^+]}+\frac{K_1K_2}{[H^+]^2}} \qquad \frac{1}{\frac{[H^+]}{K_1}+1+\frac{K_2}{[H^+]}} \qquad \frac{1}{\frac{[H^+]^2}{K_1K_2}+\frac{[H^+]}{K_2}+1}$$

- If pH << pK_1, or $[H^+] >> K_1$

1 $\qquad$ $K_1/[H^+]$ $\qquad$ $K_1K_2/[H^+]^2$

- If pK_1 << pH << pK_2, or $K_1 >> [H^+] >> K_2$

$[H^+]/K_1$ $\qquad$ 1 $\qquad$ $K_2/[H^+]$

- If pK_2,<< pH, or $K_2 >> [H^+]$

$[H^+]^2/K_1K_2$ $\qquad$ $[H^+]/K_2$ $\qquad$ 1

Substances of low solubility

- Solubility product defines the limit of solubility
  - For calcium sulfate we have:

$$K_{so} = [Ca^{+2}][SO_4^{-2}] = 10^{-4.6}$$

Solubility

- Solubility product constants
  - The solubility product constant for the dissolution of CaSO4 is about $10^{-4.6}$. If you add 100 g of CaSO4 (GFW=136) to 1 liter of water, what will the calcium concentration be?

$$K_{so} = [Ca^{+2}][SO_4^{-2}] = 10^{-4.6}$$

$$\left[Ca^{+2}\right] = \sqrt{10^{-4.6}}$$

$$[Ca^{+2}] = 10^{-2.3}\, M$$

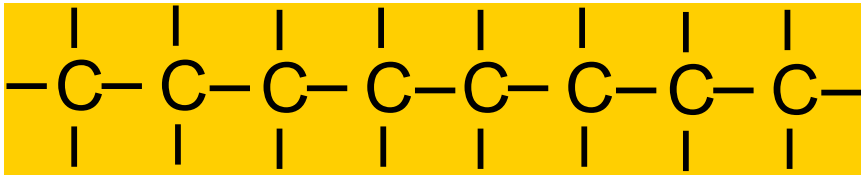
  - If you have a solution of 10^{-2} M NaSO4 which is entirely dissolved, and to this you add an excess of $CaSO_4$ crystals, how much of the calcium sulfate will dissolve at equilibrium. Present your answer in moles per liter

Organic Chemistry

- Definitions & Intro
- Properties and Nomenclature
  - Alkanes
  - Alkenes
  - Alkynes
  - Alicyclics
  - Aromatics
  - Functional Groups

Nomenclature: Intro

Carbon can form a nearly limitless diversity of compounds. One reason for this is carbon's ability to bind covalently with itself in long chains:

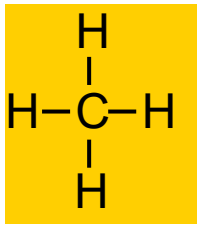


In the above structure, each carbon atom (C) is surrounded by four single bonds. This is a consequence of carbon's tendency to form four covalent bonds each. These extra bonds not used to join the carbon chain may be linked to hydrogen atoms or other structures. The particular structure shown above is an aliphatic chain. The carbons are linked in a linear fashion, without forming rings or cycles.

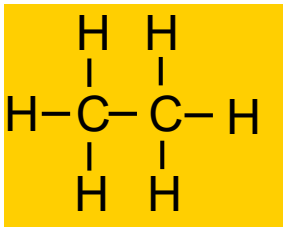
Nomenclature: Alkanes

1. Unbranched Alkanes

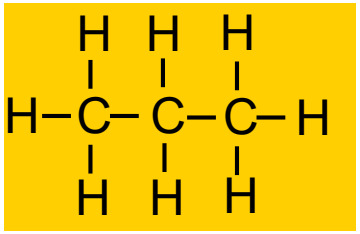
An homologous series of simple aliphatic organic compounds is then the following:



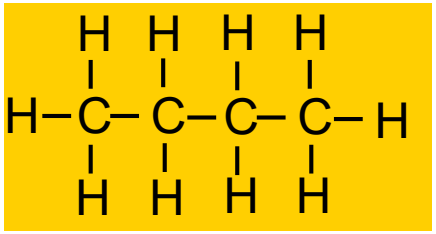
Methane



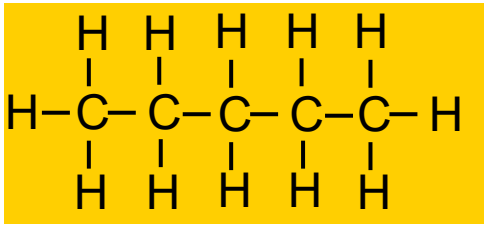
Ethane



Propane



Butane



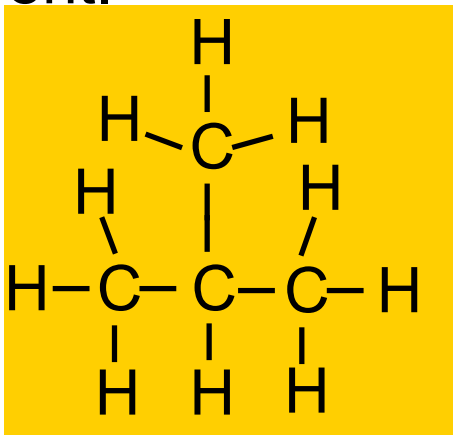
Pentane

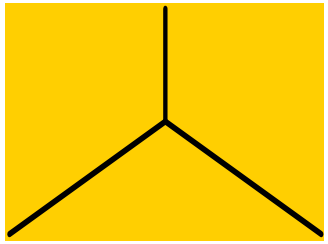
The series continues: hexane (6C), heptane (7C), octane (8C), nonane (9C), decane (10C), etc.. All alkanes have the general empirical formula, C_nH_{2n+2}.

Nomenclature: Branched Alkanes

2. Branched Alkanes & IUPAC Nomenclature

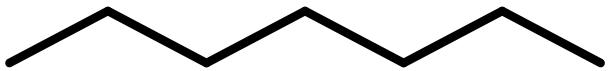
The smallest branched aliphatic is called Isobutane because it is an isomer of butane (often referred to n-butane to distinguish it from isobutane). An isomer is a compound with an empirical formula identical to a second compound, but with a different structure (i.e., geometric arrangement of the atoms) is different.



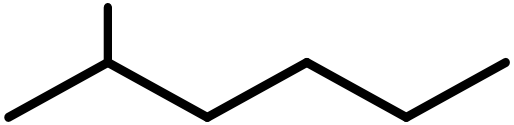


Shorthand version

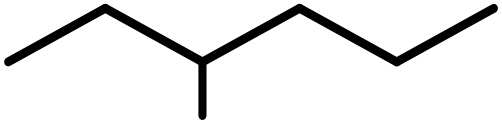
Nomenclature: Position



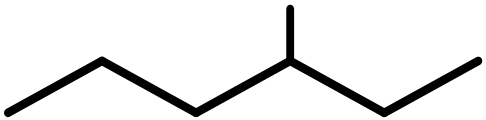
n-Heptane



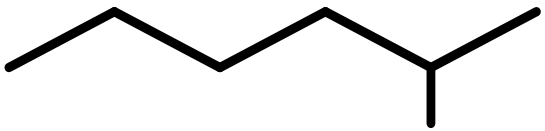
2-Methylhexane



3-Methylhexane



3-Methylhexane



2-Methylhexane

Nomenclature: Alkenes

3. Alkenes

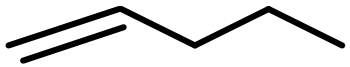
If one were to remove two hydrogens from each of the alkanes, leaving a carbon-carbon double bond in their place, one would have the series known as alkenes or olefins. Organic compounds such as these having double or triple bonds are often referred to as unsaturated, because they have less than the maximum possible number of hydrogens.

Ethene

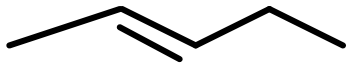
Propene

1-Butene

2-Butene



1-Pentene



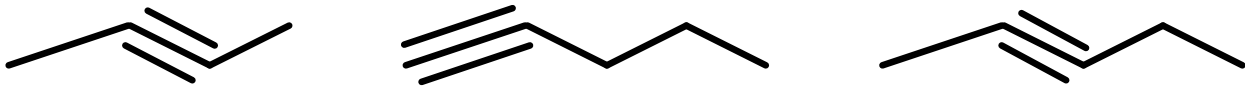
2-Pentene

Nomenclature: Alkynes

4. Alkynes

Removal of 4 hydrogens from two adjoining carbons in an alkane results in the formation of a carbon-carbon triple bond. The homologous series of these compounds is termed the alkynes (suffix -yne) and has the general empirical formula, C_nH_{2n-2}.

Ethyne **Propyne** **1-Butyne**

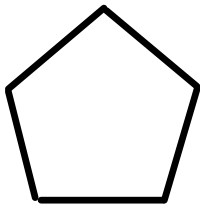


2-Butyne **1-Pentyne** **2-Pentyne**

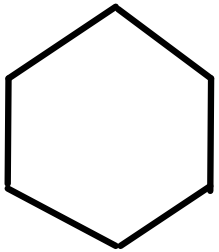
Nomeclature: Alicyclics

5. Alicyclic Hydrocarbons

When hydrocarbon chains are joined to make a ring, they are said to be cyclic, or more properly, alicyclic. They may also have double and triple bonds (e.g., cycloalkenes, cycloalkynes, in addition to cycloalkanes). Alicyclic compounds are often given the prefix, "cyclo". These compounds have the general empirical formula, C_nH_{2n}.



Cyclopentane

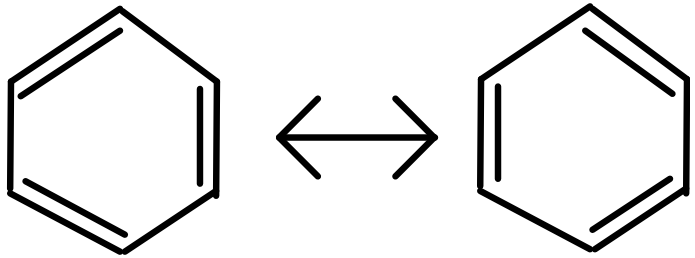


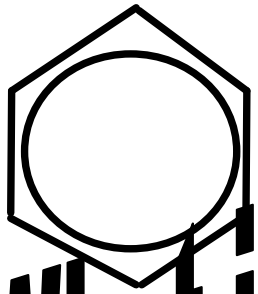
Cyclohexane

Nomenclature: Aromatics

6. Aromatics

Six-membered rings containing three alternating double and single bonds are given a special name, aromatic. These compounds are especially stable. The simplest aromatic compound is benzene.

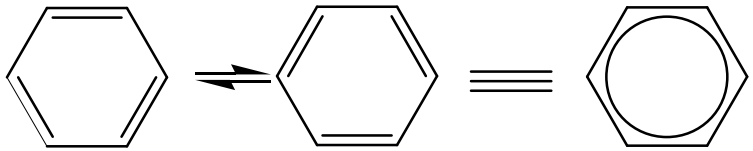




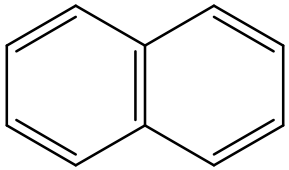
Question: What is BTEX?

Aromatics

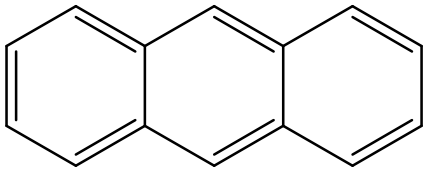
- Kekulé resonance structures of benzene



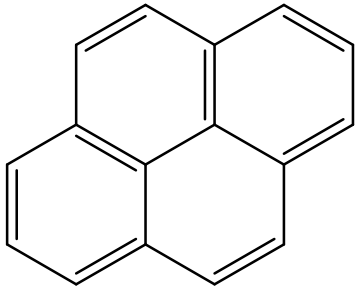
- Polynuclear (or Polycyclic) Aromatic Hydrocarbons (PAHs)



Naphthalene

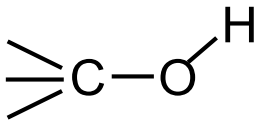
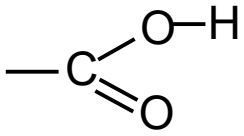
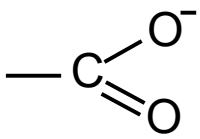
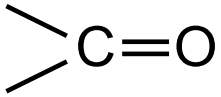
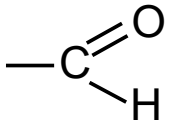
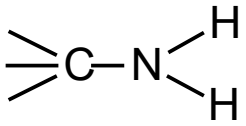


Anthracine

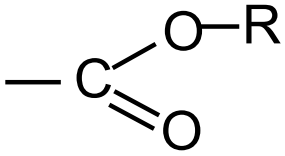
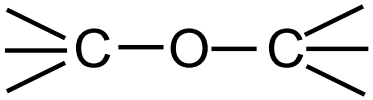
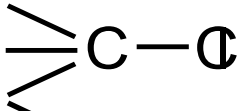
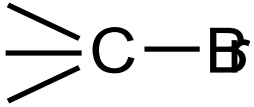
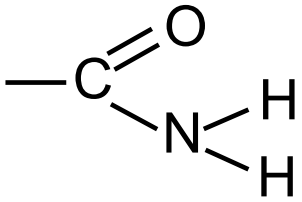
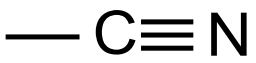


Pyrene

Nomenclature: Funct. Groups 1

Name	Structure	Suffix/Prefix
Alcohols		-ol
Acids		-oic acid
		-ate
Ketones		-one
Aldehydes		-al
Amines		-yl amine

Nomenclature: Funct. Groups 2

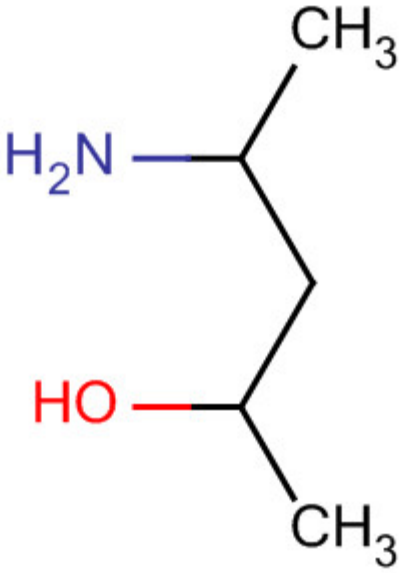
Name	Structure	Prefix/Suffix
Esters		Alkyl(R) __-at
Ethers		
Halides		chloride
		bromide
Amide		
Nitriles		-nitrile

Nomenclature question #1

- What is this called?
  - A. Chloromethane
  - B. Chlorobenzene
  - C. Chlorobenzoic acid
  - D. Chlorohydroxyethane
  - E. None of the above

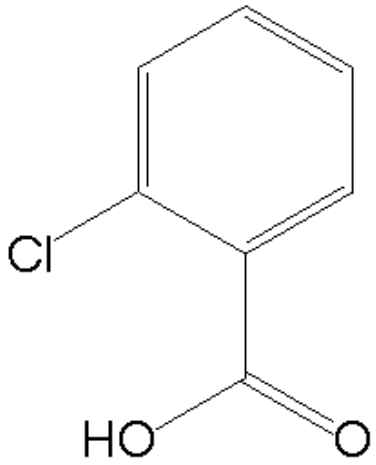
Nomenclature question #1

- What is this called?
  - A. 2-propanoate
  - B. 1,4-hydroxbutamine
  - C. Pentane-3-al
  - D. 1,5-hydroxybutamine
  - E. 4-amino-2-pentanol



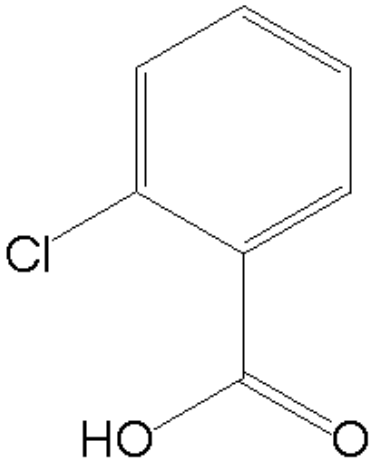
Nomenclature question #2

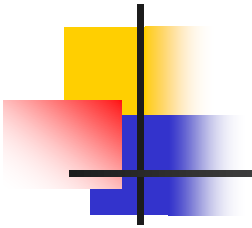
- What is this called?
  - A. Chloromethane
  - B. Chlorobenzene
  - C. Chlorobenzoic acid
  - D. Chlorohydroxyethane
  - E. None of the above



Nomenclature question #3

- What is this called?
  - A. 1-Chlorobenzoic acid
  - B. 2-Chlorobenzoic acid
  - C. 3-Chlorobenzoic acid
  - D. 4-Chlorobenzoic acid
  - E. 5-Chlorobenzoic acid





- To next lecture