Organic Chemistry 1
Lecture 2

Instructor: Prof. Duncan Wardrop

Time/Day: T & R, 12:30-1:45 p.m.

January 12, 2010

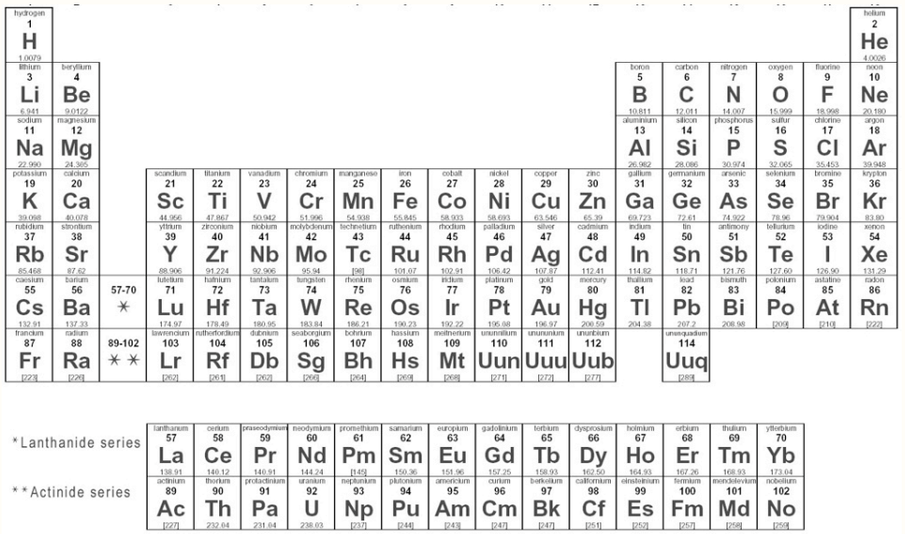
Miss the First Lecture? Go to:

http://www.chem.uic.edu/chem232

- ☑ Syllabus
- ☑ Course Policies
- ☑ DW & TA office hours
- ☑ Lecture Slides (updated each week)
- ☑ Other Handouts
- ☑ Announcements (Course News)
- ☑ Course Calendar

Self Test Question

Which of the following ions posses a noble gas electron configuration?

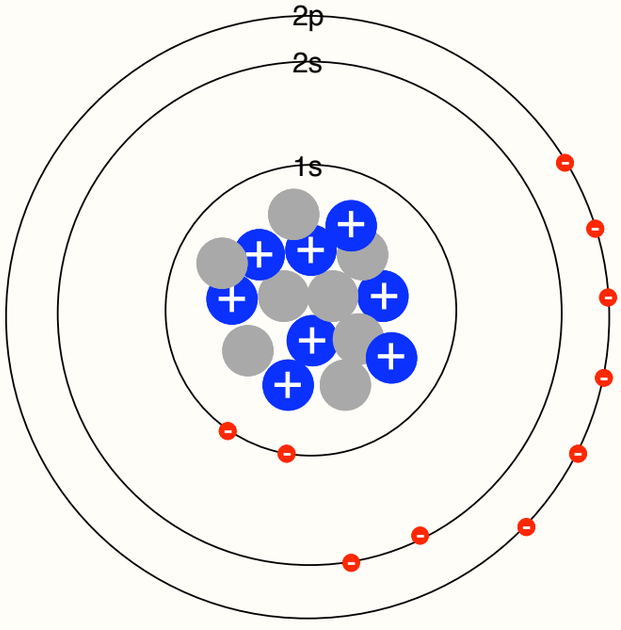


A. Mg^{+}
B. He^{+}
C. Li^{-}
D. O^{-}
E. Ca^{2+}

Formal Charge - Example 1

My logic (no memorizing equations):

1. Recognize that opposing charges cancel each other
2. Determine difference in protons vs. electrons by asking:
   - 2.a. How many *valence* (outer shell) electrons does the atom **have**?
   - 2.b. How many *valence* (outer shell) electrons does the atom "**want**" (groups #)?
3. If atom **has** more than it "**wants**," negatively charged.
4. If atom **has** less than it "**wants**," positively charged.



16
O
8

Has? =

Wants? =

Difference? =

Formal Charge - Example 1

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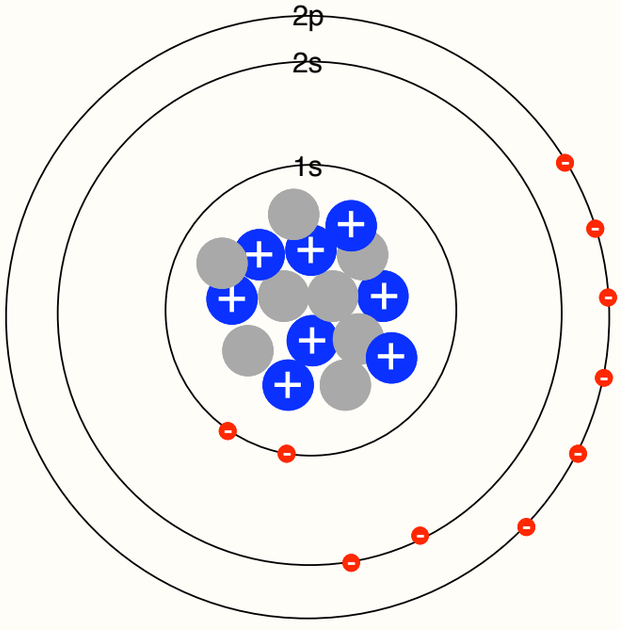

16

O

8

Has? = 8

Wants? =

Difference? =

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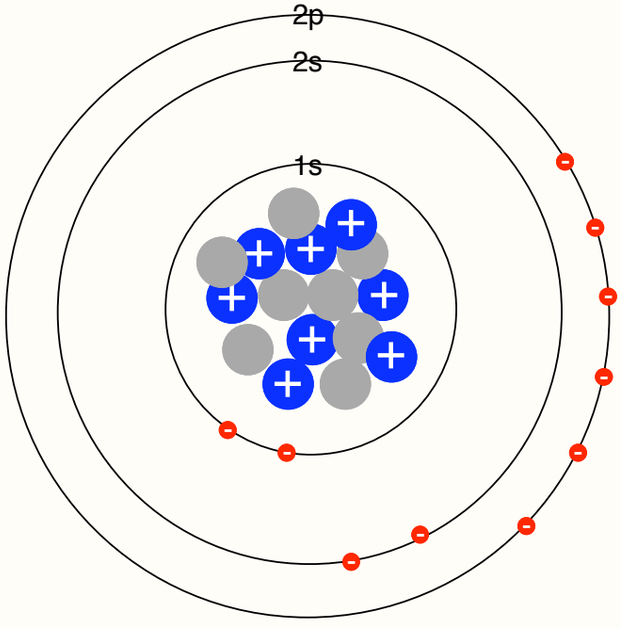

16

O

8

Has? = 8

Wants? = 6

Difference? =

Formal Charge - Example 1

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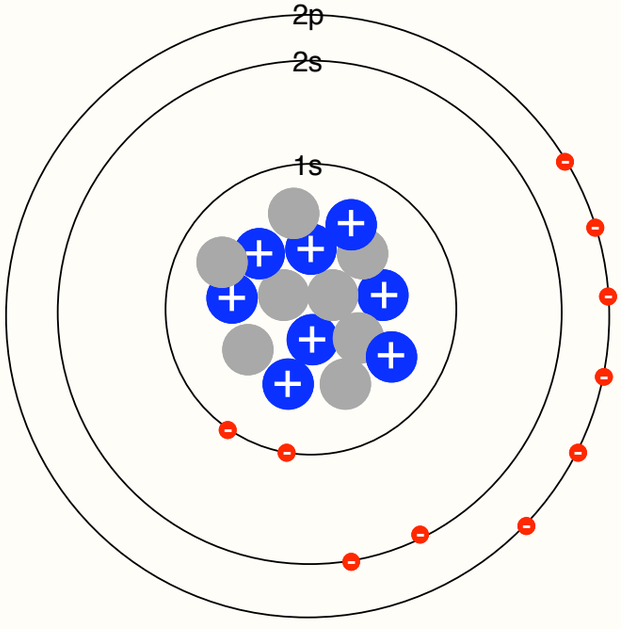

16

O

8

Has? = 8

Wants? = 6

Difference? = 2 extra

Formal Charge - Example 1

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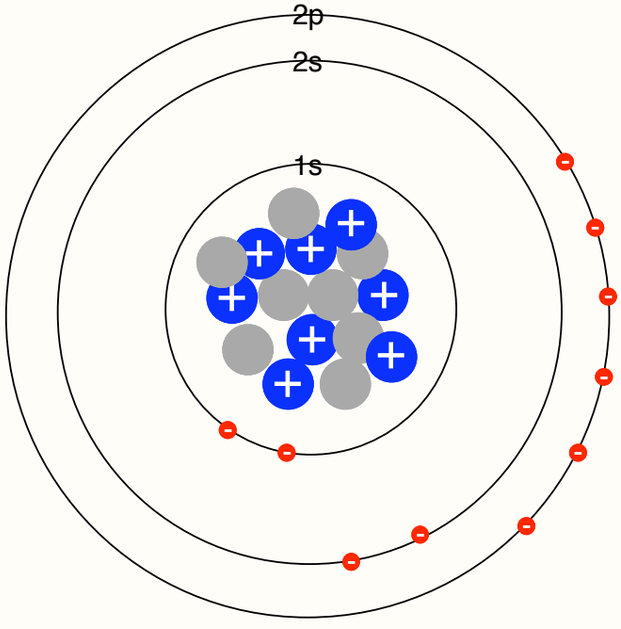

16 O 2–

8

Has? = 8

Wants? = 6

Difference? = 2 extra

Formal Charge - Example 2

My logic (no memorizing equations):

1. Recognize that opposing charges cancel each other
2. Determine difference in protons vs. electrons by asking:
   - 2.a. How many *valence* (outer shell) electrons does the atom **have**?
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If atom **has** more than it "**wants**," negatively charged.

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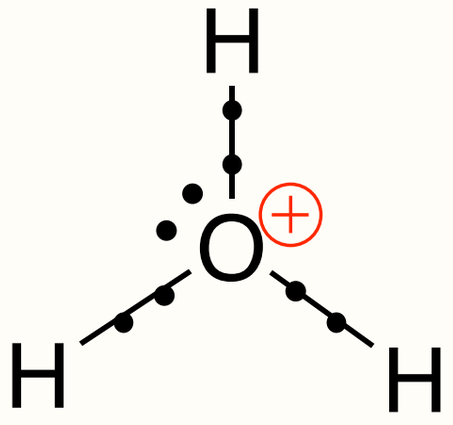

Has? =

Wants? =

Difference? =

"formal" = count one electron for each bond

Formal Charge - Example 2

My logic (no memorizing equations):

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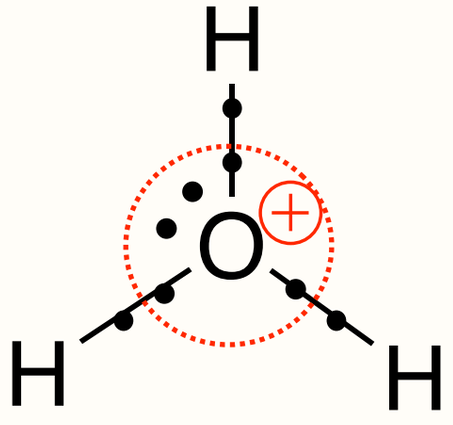

Has? = 5

Wants? =

Difference? =

"formal" = count one electron for each bond

Formal Charge - Example 2

My logic (no memorizing equations):

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   - 2.a. How many *valence* (outer shell) electrons does the atom **have**?
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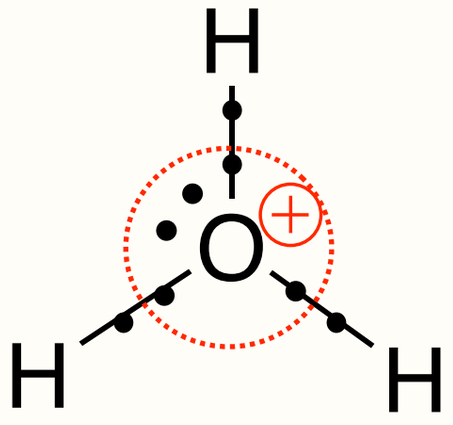

Has? = 5

Wants? = 6

Difference? =

"formal" = count one electron for each bond

Formal Charge - Example 2

My logic (no memorizing equations):

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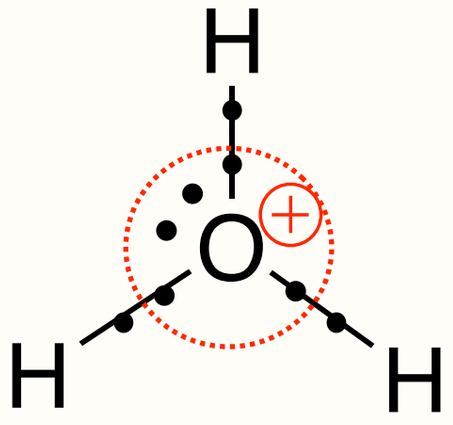


Has? = 5

Wants? = 6

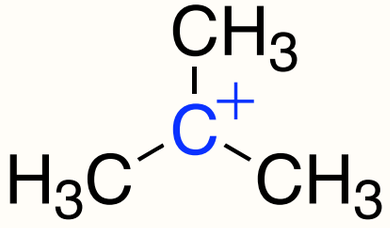
Difference? = 1 less

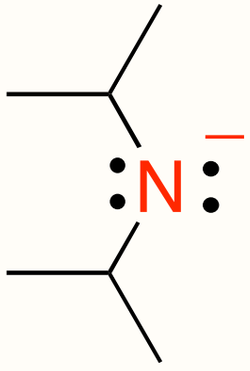
"formal" = count one electron for each bond

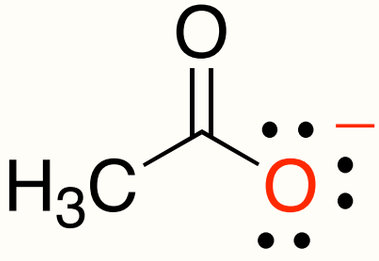
Shortcut for Some 1st and 2nd Period Atoms

Atom	Bonds Formed	Group
H	I	I
C	4	IV
N	3	V
O	2	VI
F (X)	I	VII

- For each additional bond = +I
- For each "missing" bond = –I

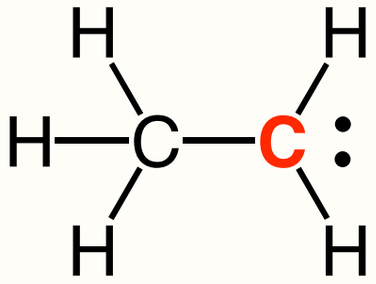


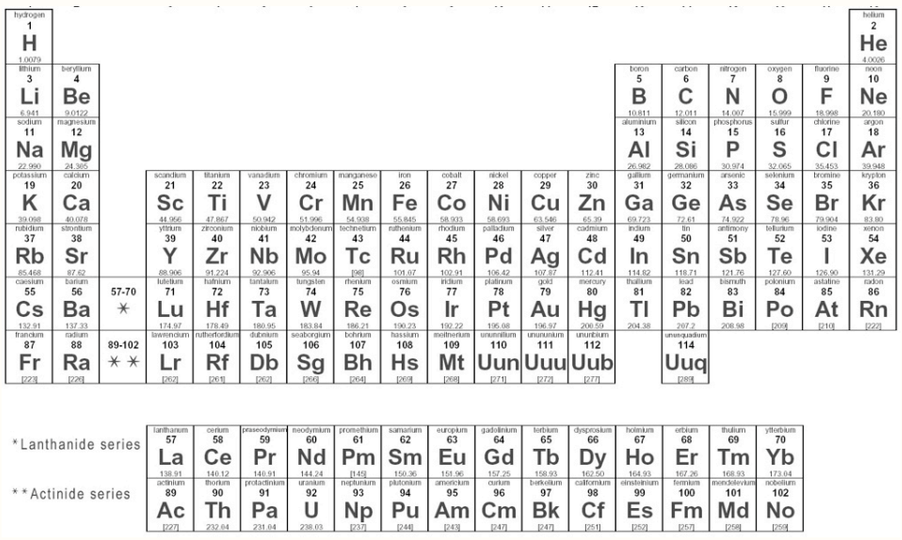




Self Test Question

What is the formal charge on the carbon atom in red?

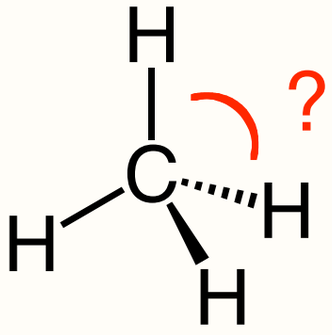




A. -2
B. -1
C. 0
D. +1
E. +2

Self Test Question

According to VSEPR, what is the bond angle between 2 H-atoms in methane (below)?



A. 105°
B. 109.5°
C. 107°
D. 180°
E. 120°

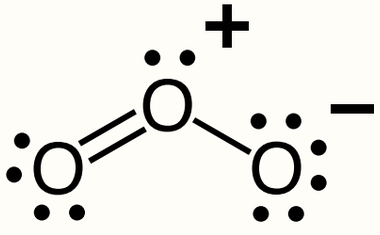
Structure and Bonding: Resonance

Section: 1.8, 1.11

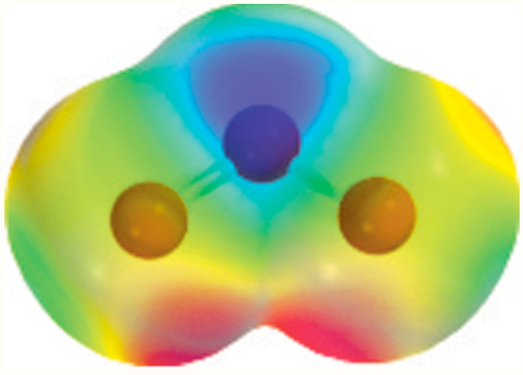
You are responsible for Section 1.10.

The Contradictory Case of Ozone

Lewis Structure suggests ozone is *non-symmetrical*



electrostatic potential map

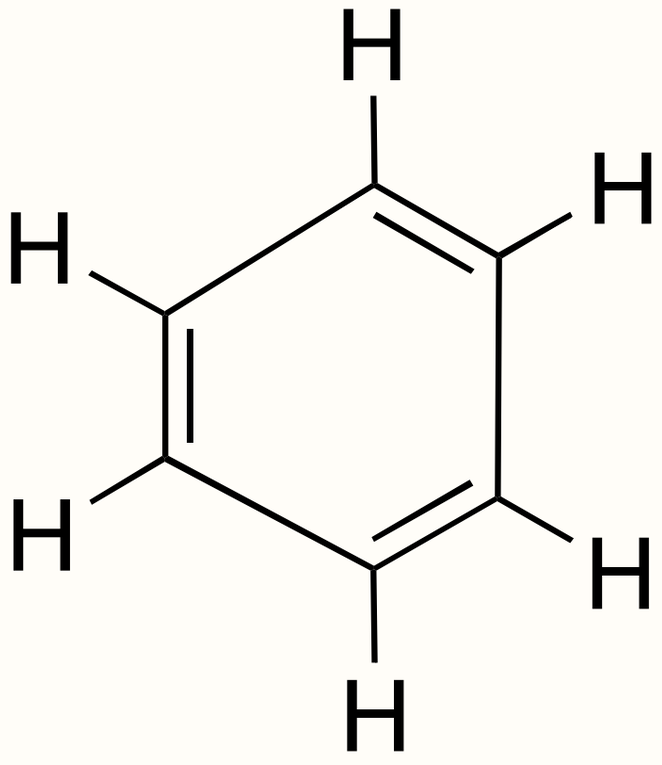


red = negative
blue = positive

Microwave spectroscopy shows that ozone is *symmetrical* (C_{2v})

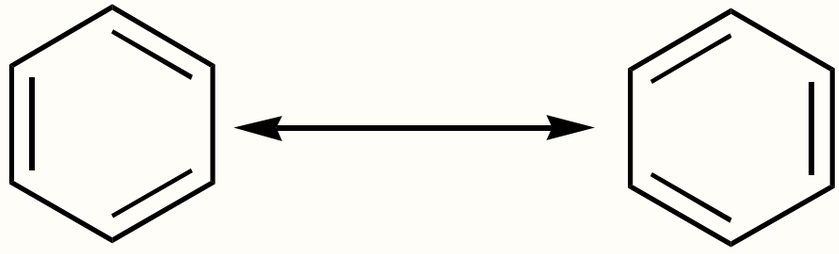
Curious Case of Benzene

Predicted



C–C bond length: 150 pm
C=C bond length: 134 pm

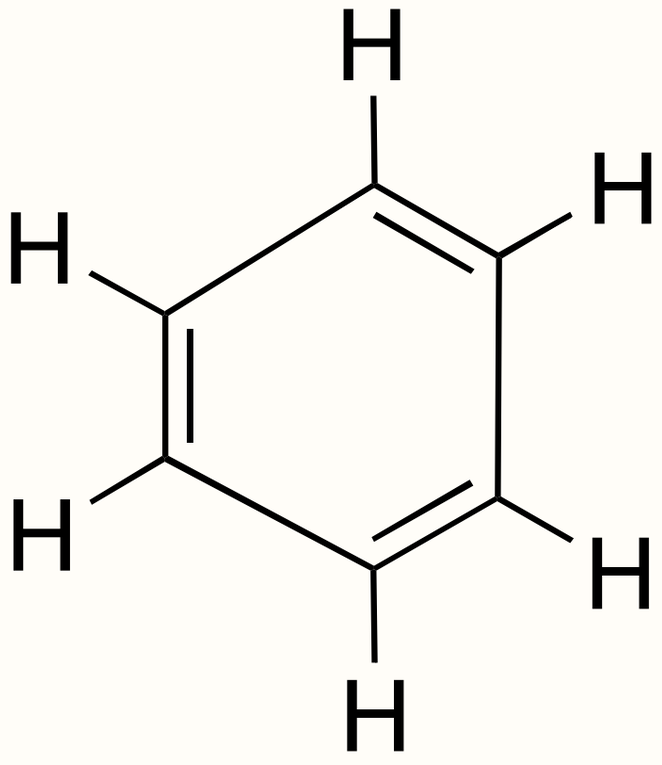
Actual



All bonds = 140 pm

Curious Case of Benzene

Predicted



C–C bond length: 150 pm
C=C bond length: 134 pm

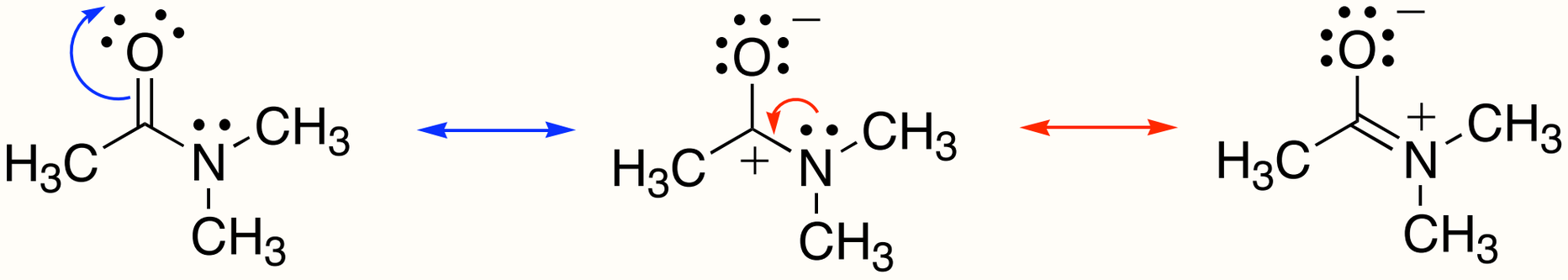
Actual

All bonds = 140 pm

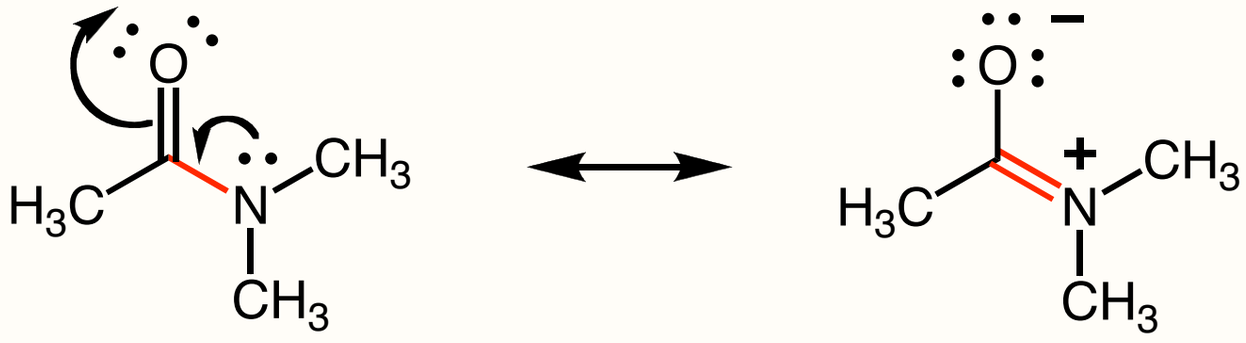
Resonance Provides the Solution

Problems:

1. Lewis structures fail to describe actual atom electron densities for molecules with more than one possible electron distribution.
2. Lewis formulas show electrons as *localized*; they either belong to a single atom (lone pair) or are shared between two atoms (covalent bond).
3. Electrons are not always *localized*; delocalization over several nuclei leads to stabilization (lower energy).



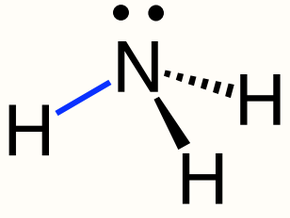
Physical Proof of Resonance in Amides

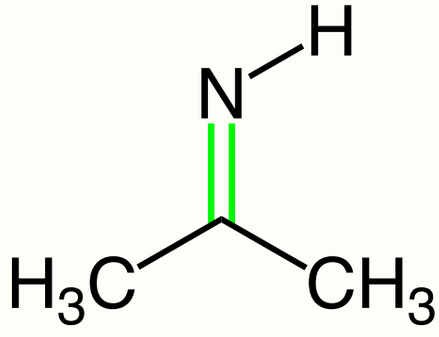


C-N (amide) Bond Length = 133 pm

C-N (amine) Bond Length = 147 pm

C=N (imine) Bond Length = 129 pm





The second amide resonance contributor suggests that amide C–N bond has partial double bond character – this has estimated to be ~40% under standard conditions. The degree to which the ionic structure contributes to the description of amides also depends on the environment surrounding the amide: the double-bonded resonance form contributes less in hydrophobic environments because the charge separation is less stabilized in non-polar solvents.

A Question of Arrows

Equilibrium between *distinct* species

Reaction from one species to another

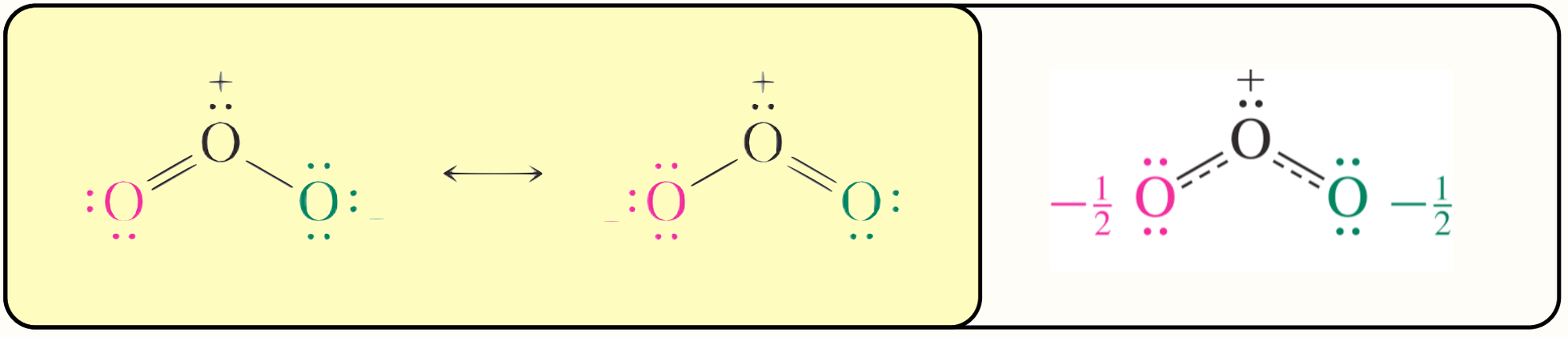
"Movement" of electrons
from donor to acceptor

Indicates that 2 species are
contributing resonance structures

Resonance

Solutions:

1. Actual molecule is considered a *resonance hybrid* (weighted average) of *contributing Lewis structures*. (Note: double headed arrow does NOT indicate interconversion.)
2. Dashed-line notation is sometimes used to indicate *partial bonds*.
3. Not all structures contribute equally.

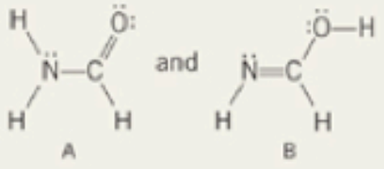


Rules of Resonance

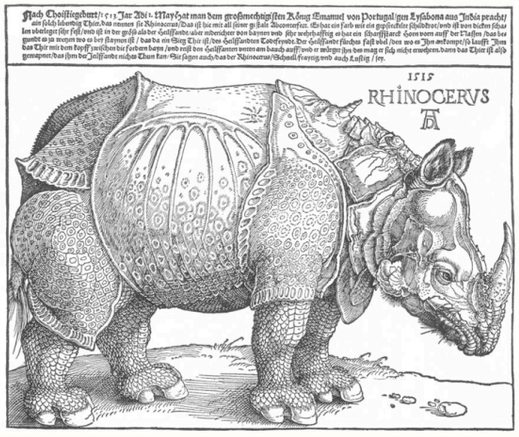
You are responsible for the "Rules of Resonance" (Pg. 27)

- How to draw resonance structures
- How to distinguish between a resonance structure and a unique electron configuration
- How to predict the major contributing structure

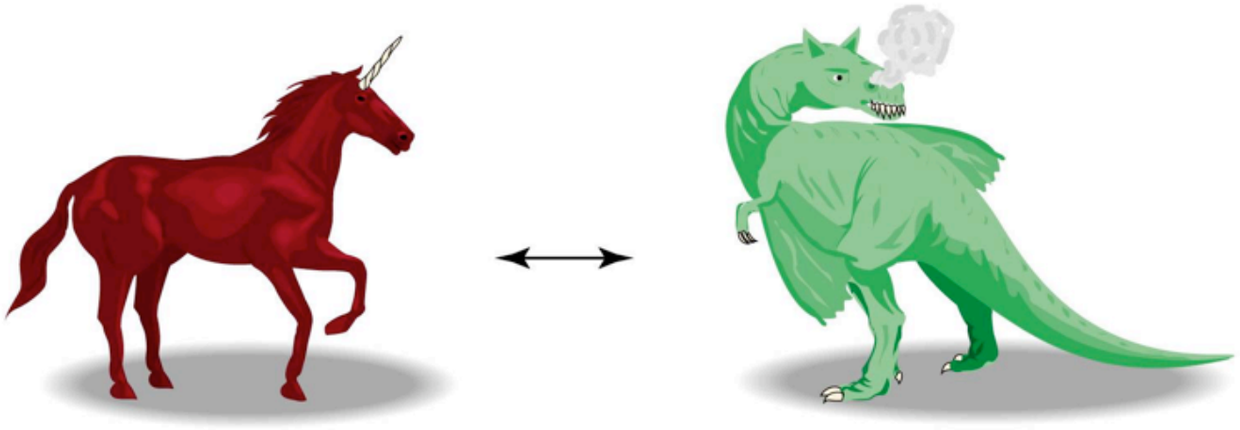
TABLE 1.6 Introduction to the Rules of Resonance

Rule	Illustration
I. *When can resonance be considered?*	
1. The connectivity must be the same in all contributing structures; only the electron positions may vary among the various contributing structures.	The Lewis formulas A and B are *not* resonance forms of the same compound. They are *isomers* (different compounds with the same molecular formula).  A B

Another Way to Think About Resonance Contributors

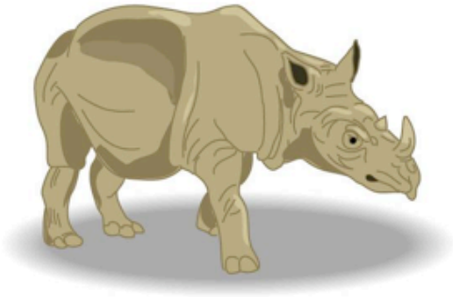


Dürer's Rhinoceros (1515 A.D.)



unicorn
resonance contributor

dragon
resonance contributor

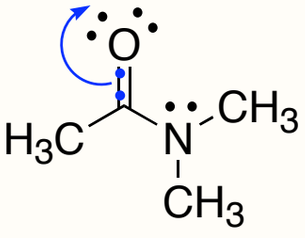


rhinoceros
resonance hybrid

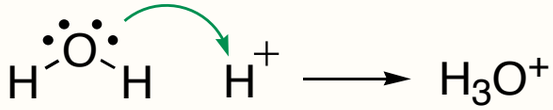
An analogy that is occasionally employed to clarify the concept of resonance contributors goes as follows: an explorer returns to his homeland from Africa and wants to describe to his countrymen the rhinoceroses that he has observed. He might describe it as a cross between a unicorn and a dragon. Unicorns and dragons do not even exist in real life and yet for the purposes of describing and understanding a rhino, it might be useful to represent it as either a unicorn or as a dragon.

Curved Arrow Notation

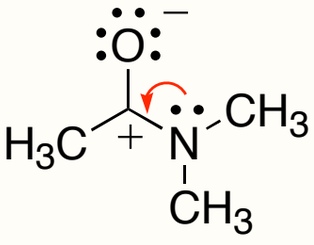
curved arrows show the movement of electrons; never atoms



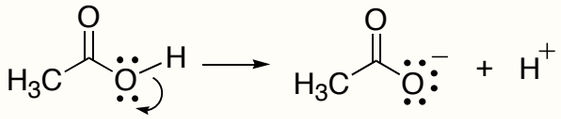
resonance: electrons in a covalent bond moving out to an atom



bond making: lone pair of electrons forming a new bond to another atom



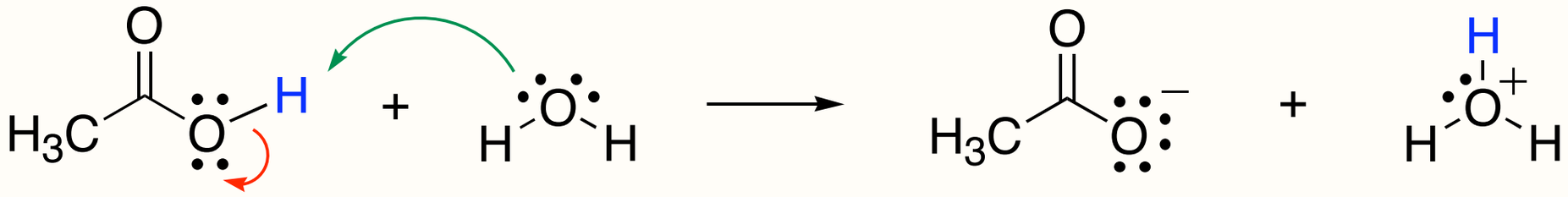
resonance: lone pair of electrons moving in between two atoms to form a new covalent bond



bond breaking: electrons in a bond leaving to most electronegative atom

Preview: Curved Arrows in Reaction Mechanisms

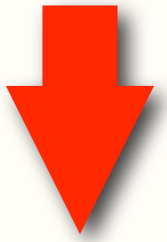
bond making



bond breaking

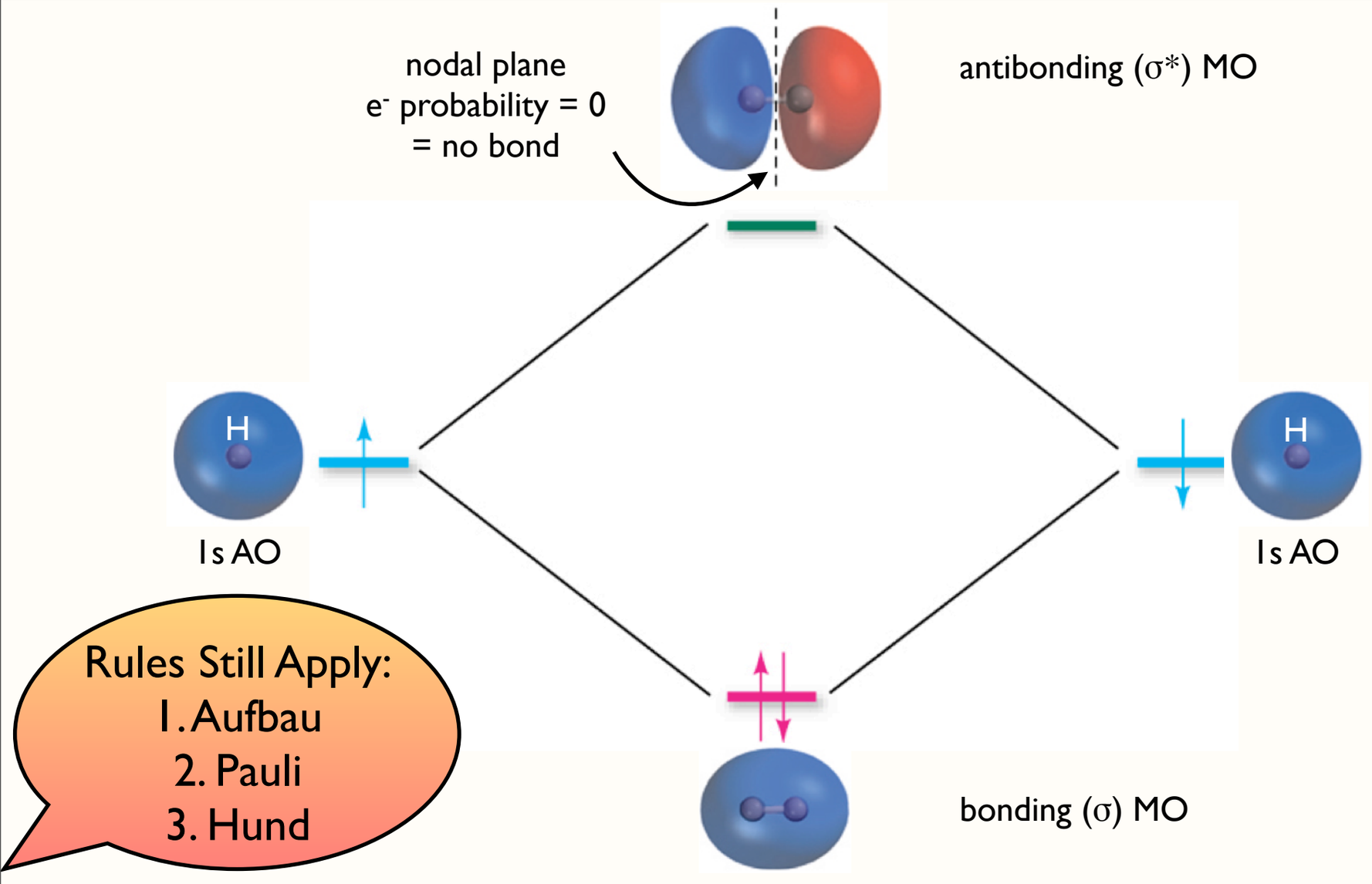
Another Way of Viewing Arrow-Pushing

Remember that curly arrows originate from e-donors (nucleophiles) and terminate at e-acceptors (electrophiles)



From an M.O. perspective curly arrows originate from filled orbitals (nucleophiles) and terminate at empty orbitals (electrophiles) - *bonds are formed from the mixing of filled and empty orbitals*

Molecular Orbital Diagram



Rules Still Apply:
1. Aufbau
2. Pauli
3. Hund

Self Test Question

Which of the following is *not* descriptive of resonance as it pertains to organic chemistry*?*

A. stabilization of negative charge
B. movement of atoms
C. delocalization of electrons
D. involves bond-breaking
E. involves bond-making

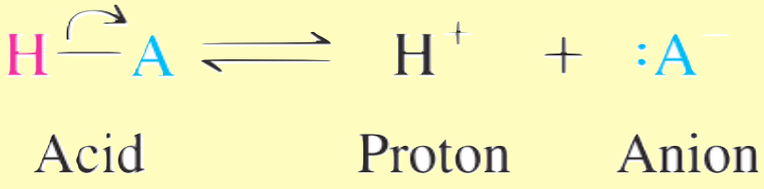
How Structure Affects Physical Properties: Acid Strength

Sections: 1.12-1.16

You are responsible for Section 1.17

Arrhenius Acids and Bases

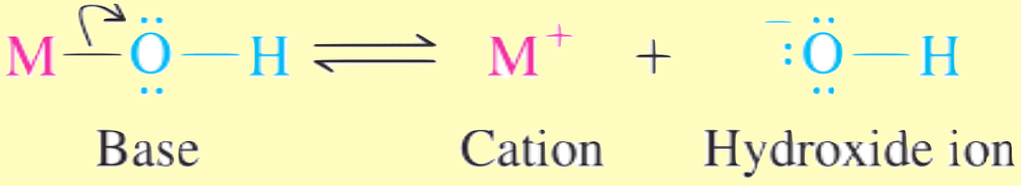
Acid: Dissociates to provide protons (H^+) in water.



strong acid: ionizes completely

weak acid: does not ionize completely

Base: Dissociates to provide hydroxide (OH^-) in water.



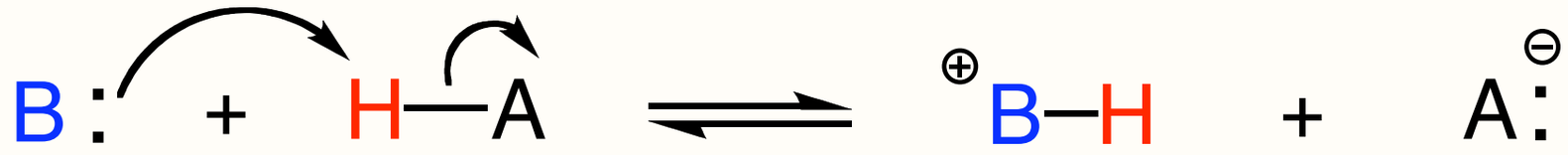
strong base: ionizes completely

weak base: does not ionize completely

According to Arrhenius, an acid is defined as a substance, which when dissolved in water, increases the concentration of protons (H+): a prime examples of such as acid include HCl and sulfuric acid. An Arrhenius base is any substance, which when dissolved in water, tends to increase the amount of OH. These definitions are limited since they are restricted to water as the solvent.

Brønsted-Lowry Acids & Bases

Acid: Proton (H+) donor
Base: Proton (H+) acceptor



Base Acid Conjugate Acid Conjugate Base

- definition does not depend on dissociation in water
- broader definition
- conjugate acid and base differ by only one proton
- most often used definition in this course

In 1923, Johannes Bronsted and Thomas Lowry independently proposed that an acid could be defined as a substance that is capable of donating a hydrogen ion, or proton, while a base is any molecule that can accept a hydrogen ion. In this definition, bases and acids necessarily occur as conjugate partners.

Molecular Orbital Picture

H-A Bond Breaks!

n **(B)**

Non-Bonding M.O.

σ* (H-A)

Anti-Bonding M.O.

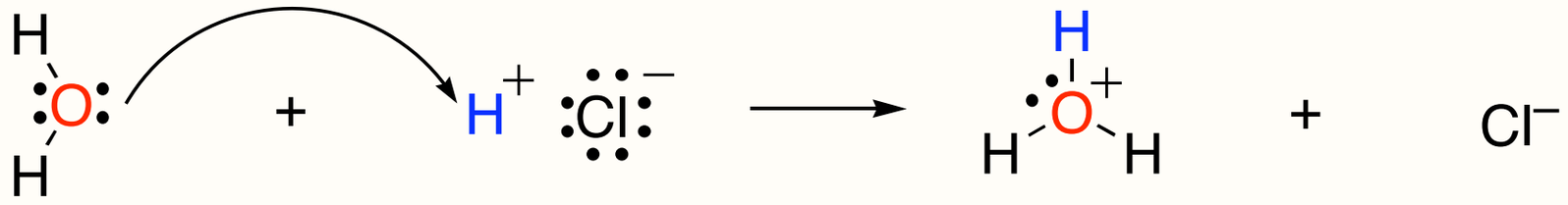
σ (B-H)

Bonding M.O.

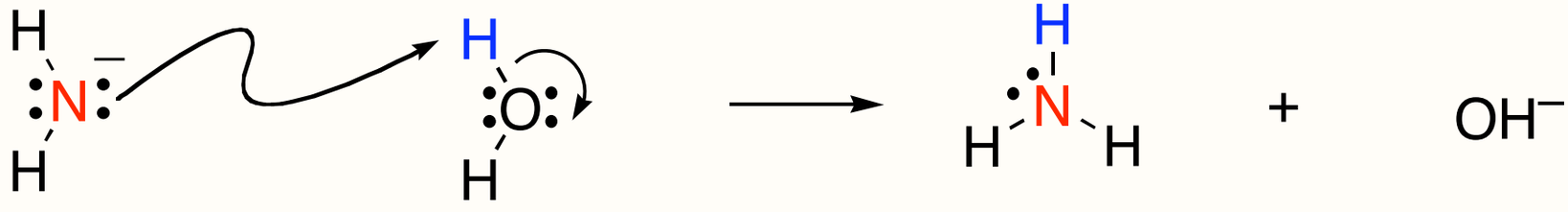
n **(A)**

Non-Bonding M.O.

Water Can Act as a Base or Acid Under Brønsted-Lowry Definition

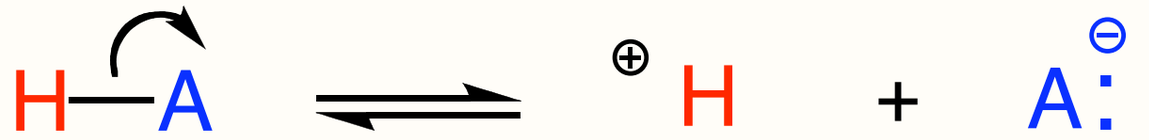


water (base) | HCl (acid) | hydronium ion (conjugate acid) | chloride ion (conjugate base)



amide (base) | water (acid) | ammonia (conjugate acid) | hydroxide ion (conjugate base)

Acid Strength is Measured by the Acid Dissociation Constant (pK_a)



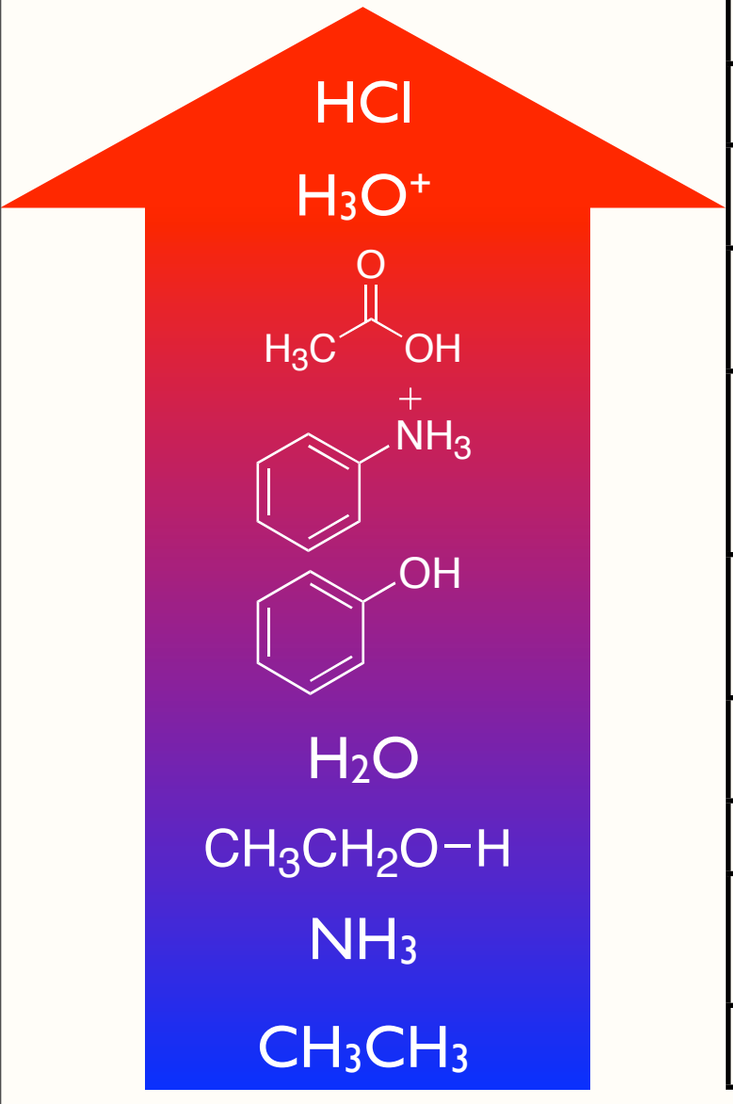
Acid Proton Anion

$$K_a = \frac{[H^+][:A^-]}{[HA]}$$

$$pK_a = -\log_{10} K_a$$

Note that the value of *K* reflects the relative thermodyamic stability of acid and anion

pKa Scale



acid	pK_a
hydrochloric	-3.9
hydronium	-1.7
acetic acid	4.7
pyridinium	5.2
phenol	10
water	15.7
ethanol	16
ammonia	36
ethane	62

Take home message: the larger the K_a value, the smaller the pK_a value, the stronger the acid.

$$HA \xrightarrow{\text{dissociation}} H^+ + A^-$$

HA: acid; A^-: conjugate base

$$pK_a = -\log_{10} \frac{[H+][A^-]}{[HA]}$$

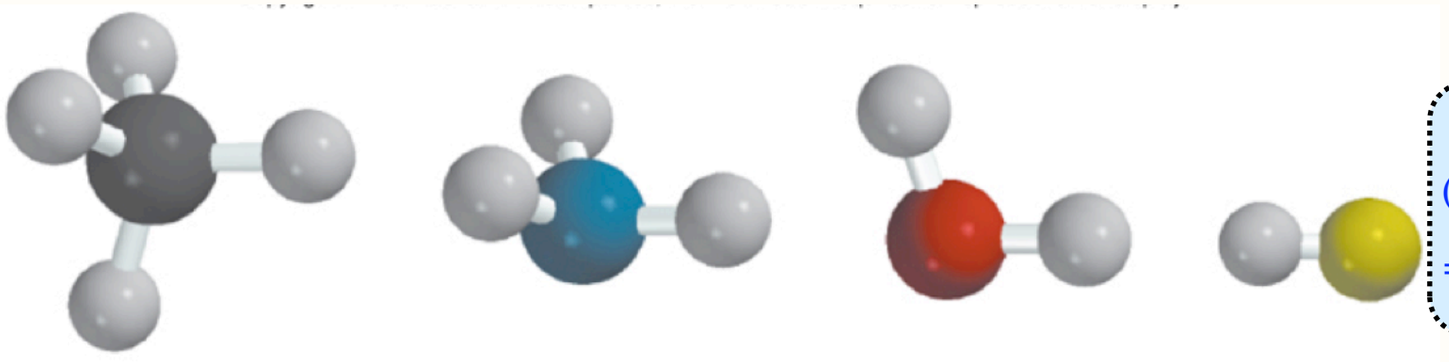
$-\log_{10}(1/100) = 2$
$-\log_{10}(1/10) = 1$
$-\log_{10}(1) = 0$
$-\log_{10}(10) = -1$
$-\log_{10}(100) = -2$

Structure Affects Acid Strength

1. Electronegativity of H-Donating Atom

- dominant effect for same periods (rows)
- more electronegative conjugate base = more stable conjugate base = Ka lies further to right
- Alternative reasoning: H of conjugate acid (HA) becomes more positive with increasing electronegativity of A

least stable (highest energy) conjugate base = weakest acid



most stable (highest energy) conjugate base = strongest acid

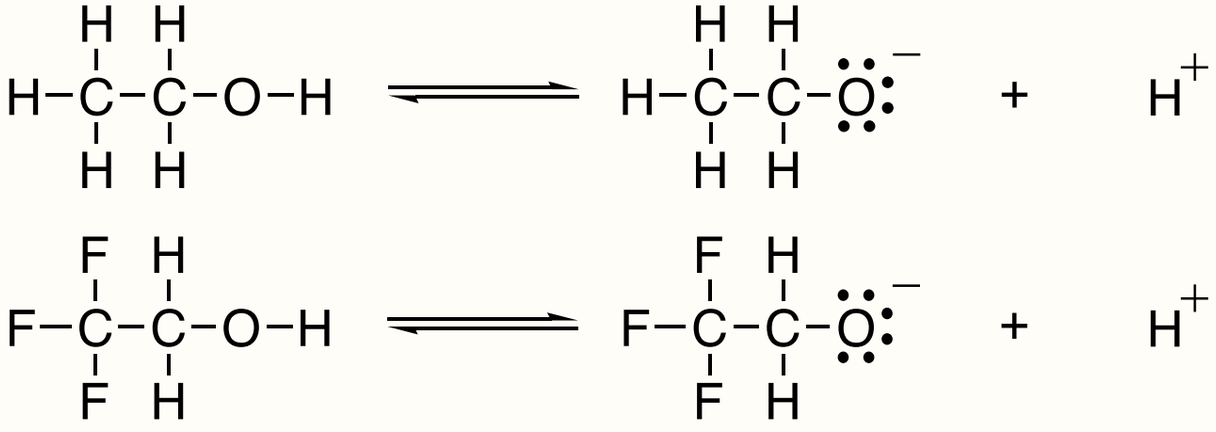
acid	CH_4	NH_3	H_2O	HF
pK_a	60	36	15.7	3.1

conjugate base $^-:CH_3$ $^-:NH_2$ $^-:OH$ $^-:F:$

Structure Affects Acid Strength

1. Electronegativity (cont.)

- inductive effect of electronegative substituents also stabilizes conj. base
- the more electronegative the group, the greater the stabilization
- the closer the electronegative group, the greater the inductive effect
- inductive effect = structural effects that are transmitted *through* bonds

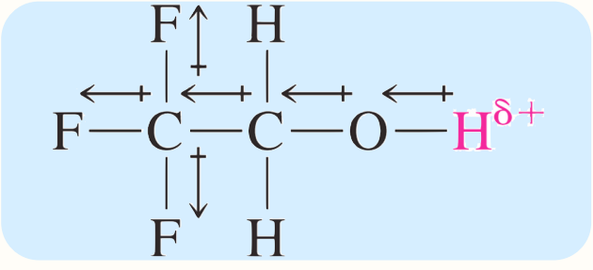


$K_a = 1 \times 10^{-16}$

$pK_a = 16$

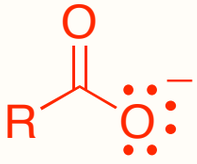
$K_a = 5 \times 10^{-12}$

$pK_a = 11.3$

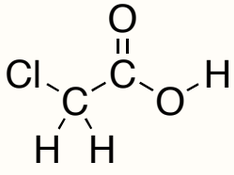


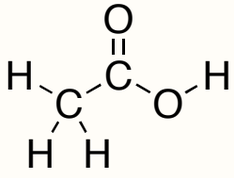
Self Test Question

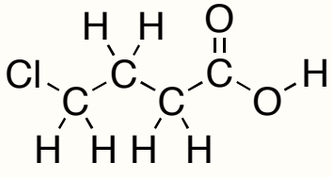
Which of the following carboxylic acids (-CO_2H) is the most acidic (lowest pK_a)?

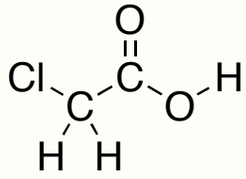


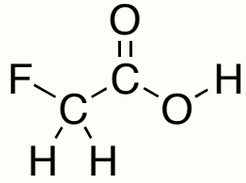
carboxylate anion
(conjugate base)

A. 

B. 

C. 

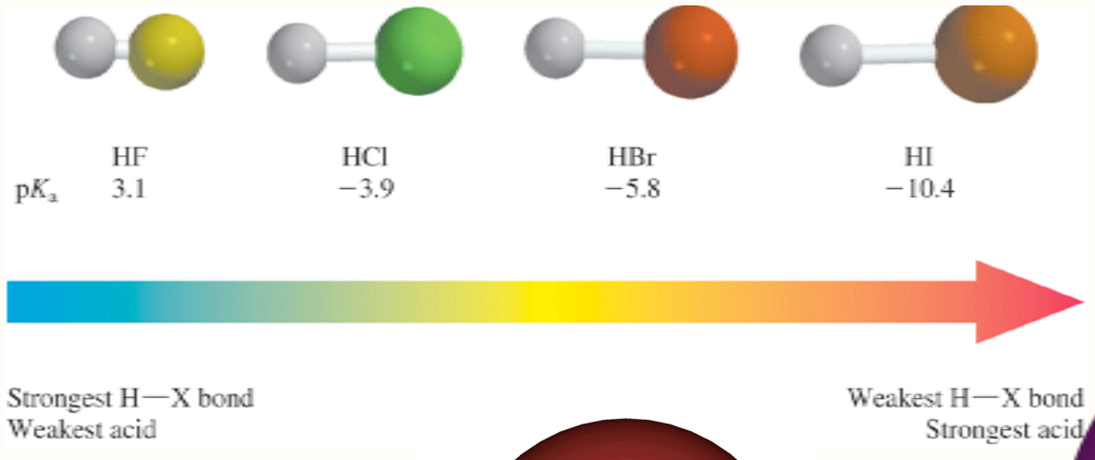
D. 

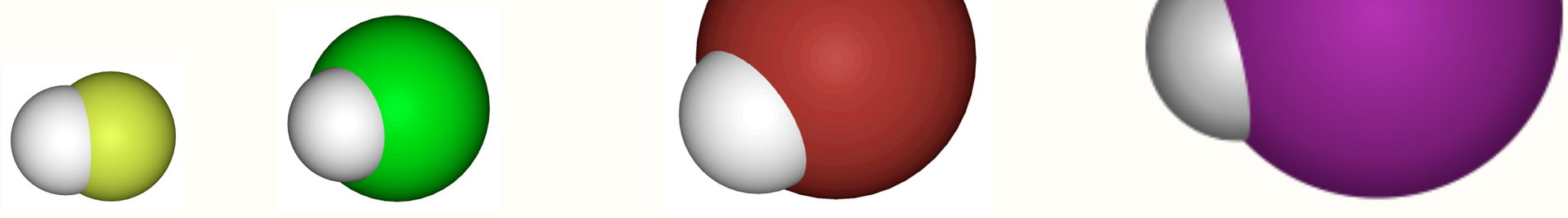
E. 

Structure Affects Acid Strength

2. Bond Strength

- dominant effect for same groups (columns)
- Similar sized bonding orbitals = better overlap = stronger bond
- Stronger H–A bond = weaker acid

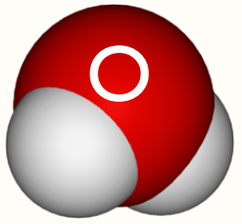




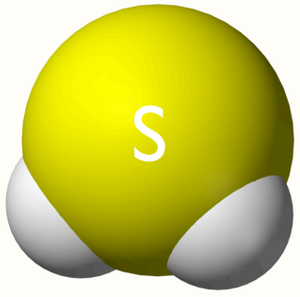
Self Test Question

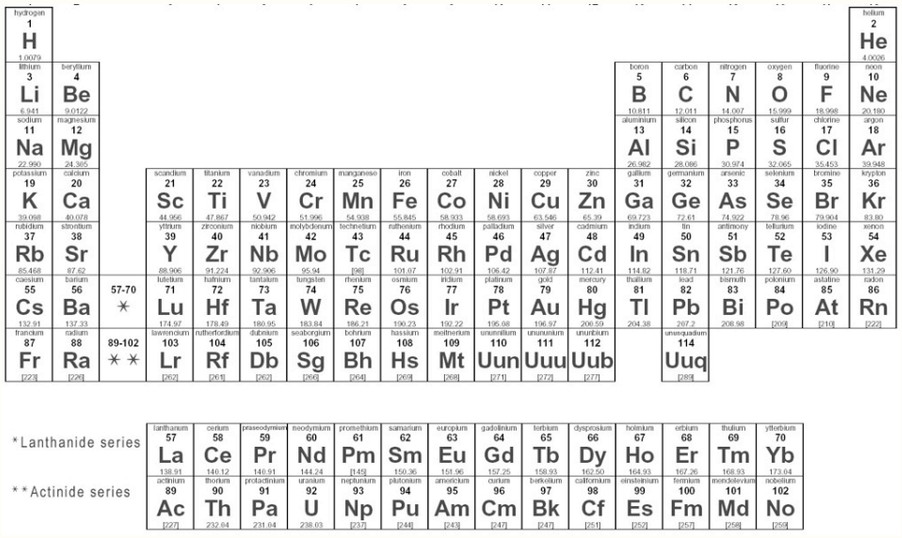
Which of the following is the strongest acid?

A. H_2O



B. H_2S

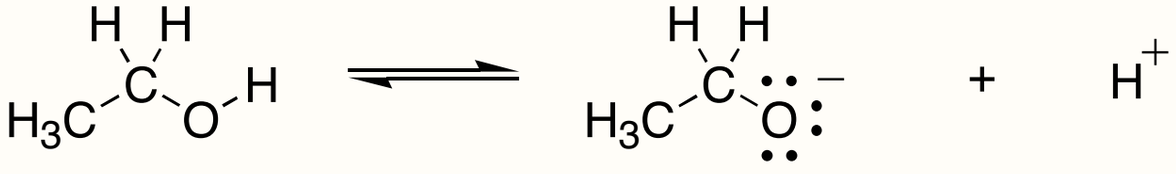




Structure Affects Acid Strength

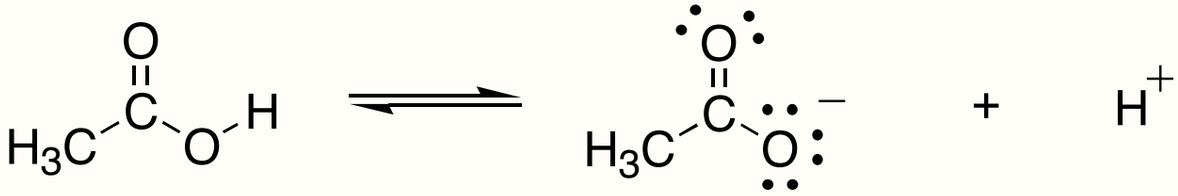
3. Resonance (delocalization of e⁻s in conj. base):

- delocalization of e⁻s in conj. base = increased stability (lower NRG) of conjugate base
- more stable conj. base = larger K_a = smaller pK_a = stronger acid



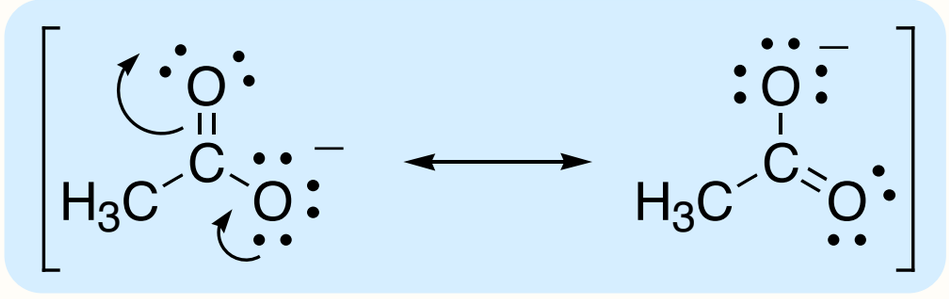
$K_a = 1 \times 10^{-16}$

pK_a = 16



$K_a = 2.0 \times 10^{-5}$

pK_a = 4.7



Acid-Base Equilibria: Determining the Direction of Acid-Base Reactions

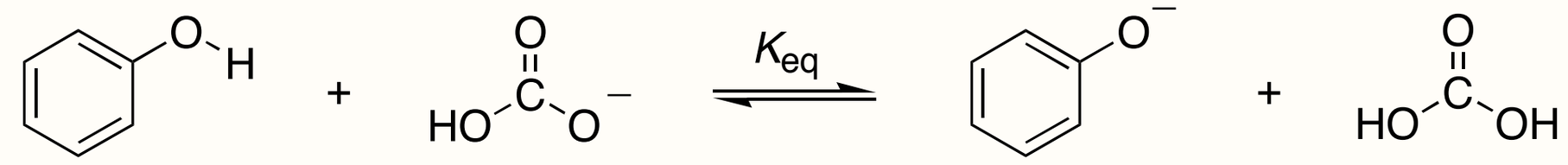
You must identify the *ACID* on each side of the equilibrium:

$pK_{eq} = pK_a$ (acid left) - pK_a (acid right)

$K_{eq} = 10^{-[pKa \text{ (acid left)} - pKa \text{ (acid right)}]}$

- remember: $p = -\log_{10}$
- this equation works for any acid-base reaction; doesn't matter which way equilibrium is written

Example:



phenol (pK_a = 10) — acid

hydrogen carbonate (pK_a = 10.2) — base

phenoxide anion (pK_a = NA) — base

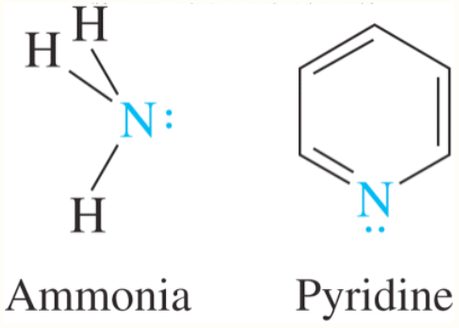
carbonic acid (pK_a = 6.4) — acid

$$K_{eq} = 10^{-[10 - 6.4]} = 10^{-[3.6]} = 2.5 \times 10^{-4}$$

since K_{eq} <1, then equilibrium lies to the left

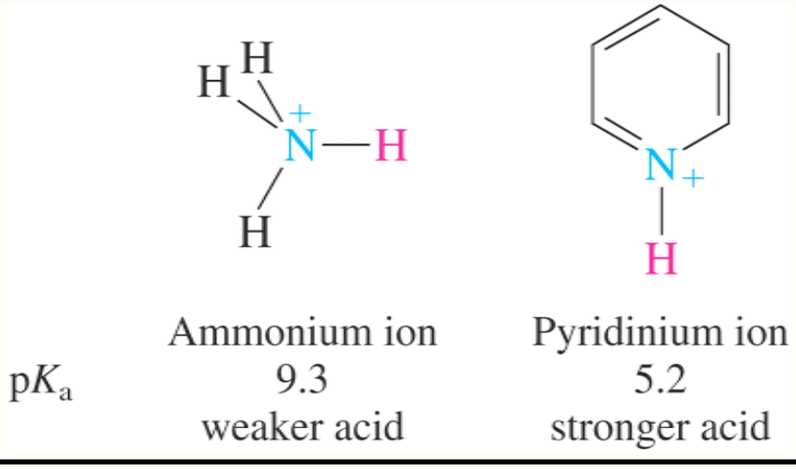
Finally, What About Strengths of Bases?

Question: Is ammonia or pyridine a stronger base?



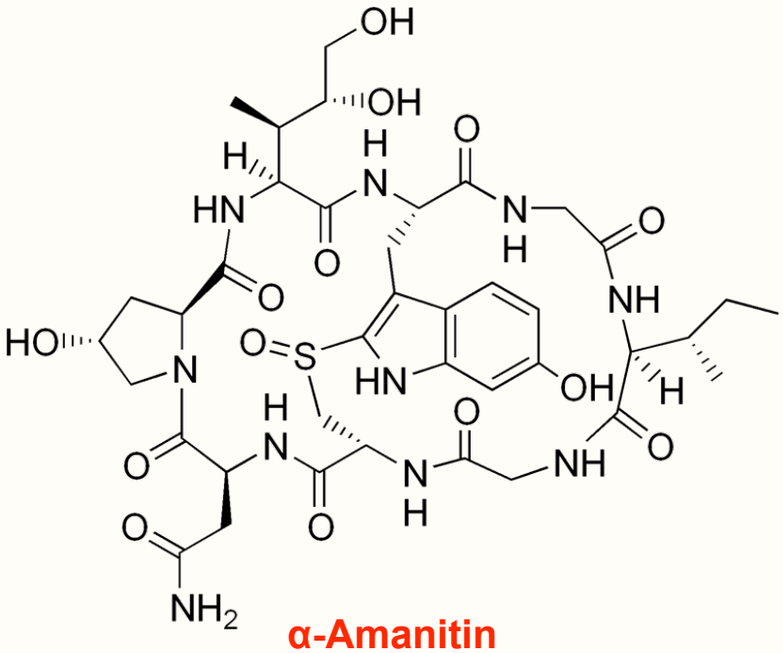
Solution:

1. Determine which conjugate acid of each base is the weakest.
2. The weaker the conjugate acid, the stronger the conjugate base.

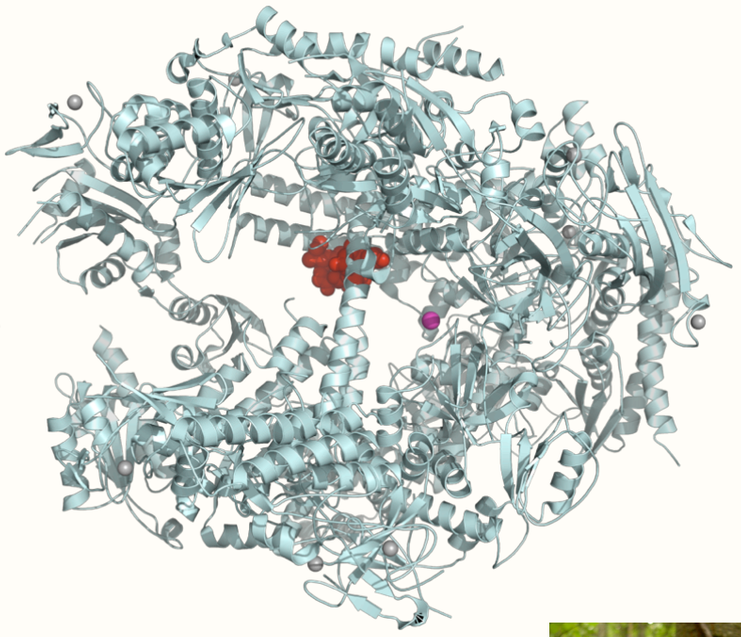


Molecule of the Week...α-Amanitin
Be Careful What You Eat (and Who You Marry)!

Amanita phalloides



α-Amanitin



α-Amanitin (red) bound to RNA polymerase II

Tiberius Claudius Caesar Augustus Germanicus (10 B.C.–A.D. 54)

Read more about the death of Claudius.....

Amanita caesarea

α-Amanitin, a cyclic peptide comprised of eight amino acids, is widely regarded as among the most lethal of all natural products. This notorious toxin is isolated from the fungus *Amanita phalloides*, more commonly known as the Death Cap, and has an oral LD50 of 0.1 mg/kg. In light of this toadstool's similarity to a number of edible mushrooms, including the highly prized *Amanita caesarea,* it has been involved in the majority of human deaths from mushroom poisoning. Several historical figures are suspected victims of α-amanitin, including the Roman Emperor Claudius, who may have been poisoned by his wife Julia Agrippina. The Roman historian,

Reminder

Quiz *next* week in discussion section.

Covers *Carey* Chapter 1

Functional groups will not be examined (yet)

Next Lecture...

Sections: 2.1-2.11