Chapter 3: Polar Covalent Bonds; Acids and Bases

Concepts to Review from General Chemistry:

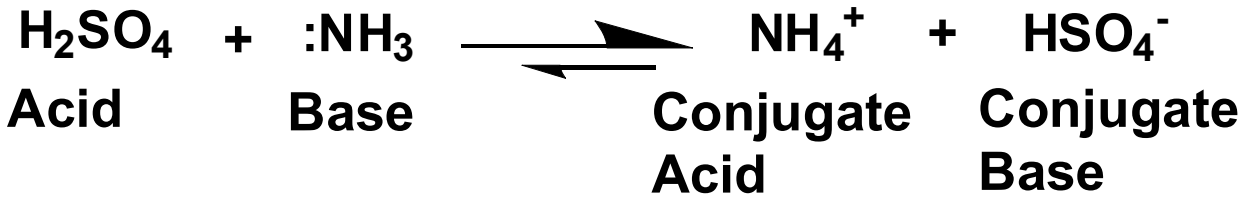
- ✓ Electronic Structure
- ✓ Molecular Orbitals and Atomic Orbitals
- ✓ Bonding and Antibonding
- ✓ Lewis, Condensed, or Kekule Structures
- ✓ Determining Formal Charge
- ✓ Resonance!!

Today –

- Brønstead-Lowry Acids and Bases
- Organic Acids and Bases
- Acid Dissociation Constants - pKa and pH
- Lewis Acids and Bases –
  - Nucleophiles and Electrophiles

Acids and Bases: pH and pKa

- A Brønsted–Lowry Acid is a species that can donate a proton.
- A Brønsted–Lowry Base is a species that can accept a proton.

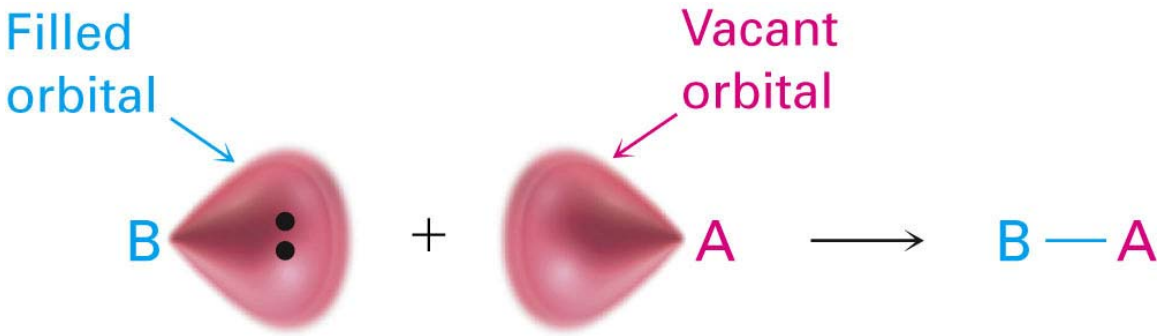


Remember ->

- Acid Base reactions are also called Proton Transfer Reactions.
- Acidity depends on medium.
- We'll always think of H_2O as standard, but often acids are less dissociated in organic solvents.

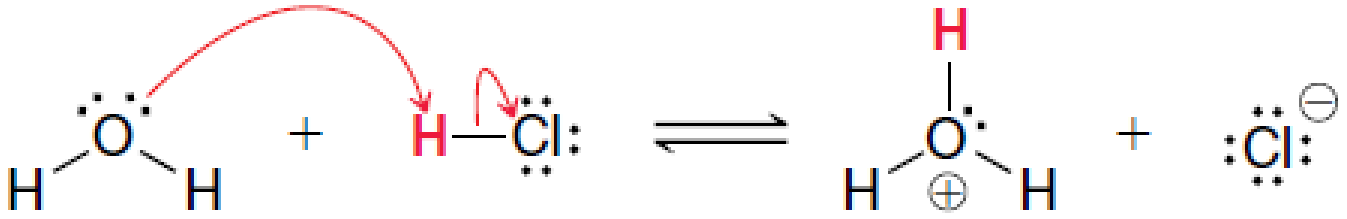
Acids and Bases: The Lewis Definition

- Lewis acids are electron pair acceptors and Lewis bases are electron pair donors
- Brønsted acids are not Lewis acids because they cannot accept an electron pair directly (only a proton would be a Lewis acid)
- The Lewis definition leads to a general description of many reaction patterns but there is no scale of strengths as in the Brønsted definition of pK_a

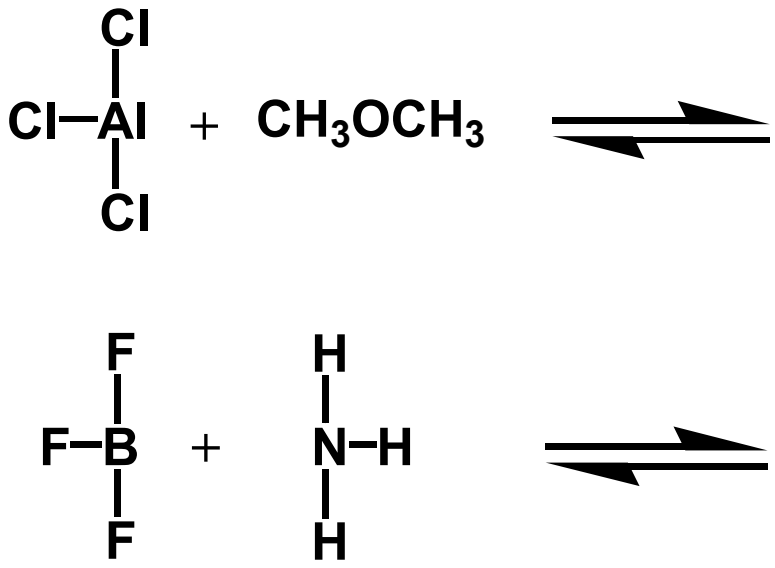


Lewis Acids and Bases

- Lewis acid/base definition:
  - A Lewis acid accepts a pair of electrons.
  - A Lewis base donates a pair of electrons.
- Acids under the Brønsted-Lowry definition are also acids under the Lewis definition.
- Bases under the Brønsted-Lowry definition are also bases under the Lewis definition.
- This reaction fits both definitions.



Lewis Acids and Bases:



- Since a Lewis acid is a species that accepts electrons, it is termed an ELECTROPHILE ('lover of electrons')
- A Lewis base is a species that donates electrons to a nucleus with an empty (or easily vacated) orbital, and is termed a NUCLEOPHILE.

Acids and Bases: pH and pKa

Remember from General Chemistry:

- The acidity of an aqueous solution is determined by the concentration of H_3O^+ ions.

- Water Autoprotolysis Constant, Kw = 1.00×10^{-14} at 24°C

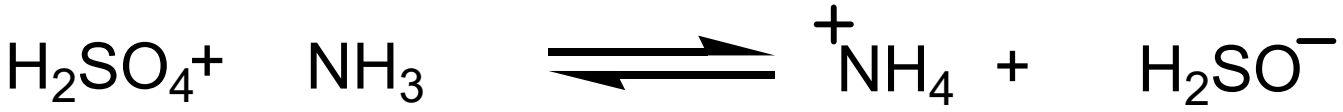
$$Kw = [H_3O^+]\,[^-OH]$$

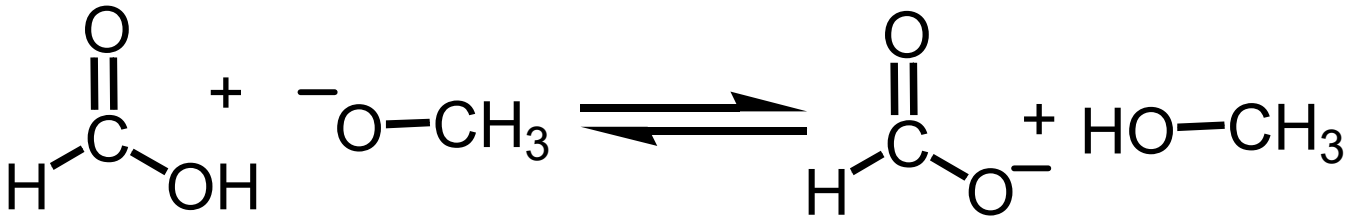
- In a neutral solution, $[H_3O^+] = [^-OH] = 1.00 \times 10^{-7}$ M

$$pH = -\log [H_3O^+]$$

- Thus, in a neutral solution – the pH is 7
- Acidic Solutions have $[H_3O^+] > 10^{-7}$ M and a pH < 7
- Basic Solutions have $[H_3O^+] < 10^{-7}$ M and a pH > 7

Acids and Bases: pH and pKa





Acids and Bases: pH and pKa

- In order to compare the reactivity of acids - what we need is a way to quantify their acid strengths.
- We can do this using the equilibrium constant for this reaction.

$$K_{eq} = \frac{[H_3O^+][A^-]}{[H_2O][HA]}$$

in H_2O, $[H_2O]$ = Constant, 55 Molar (M)

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

As with any equilibrium, the bigger the Ka the stronger the acid.

Acids and Bases: pH and pKa

- K_as typically range from 10^{14} to 10^{-50} in value.

$$pK_a = -\log K_a$$

- Low or negative pK_a means strong acid ➔weak conj. base
- High pK_a value means weak acid ➔ strong conj. Base

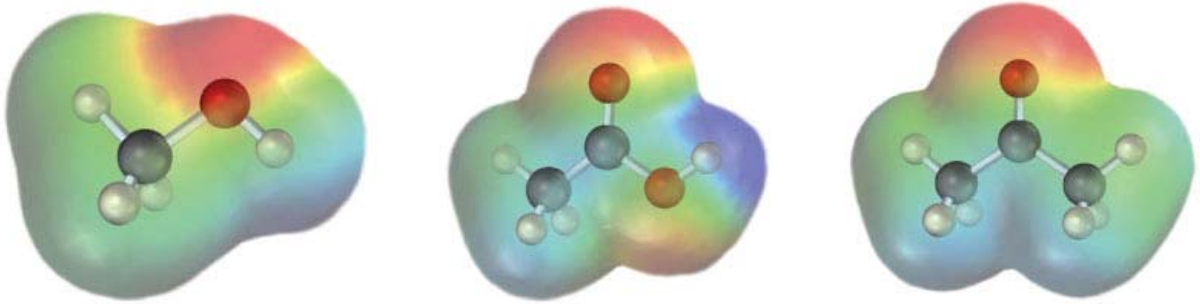
Typical values:

Strong Acid	(H_2SO_4)	$pK_a = 0$
Organic Acid	(CH_3CO_2H)	$pK_a = 4$
Organic Compound	(CH_4)	$pK_a = 40$

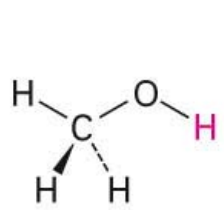
Organic Acids and Organic Bases

Organic Acids:

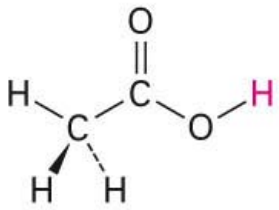
- characterized by the presence of positively polarized hydrogen atom



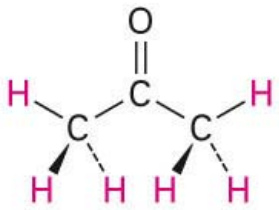
Some organic acids



Methanol
($pK_a = 15.54$)



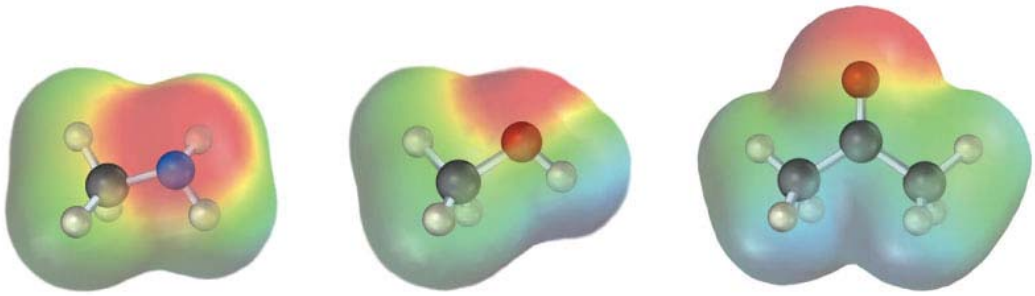
Acetic acid
($pK_a = 4.76$)



Acetone
($pK_a = 19.3$)

Organic Bases

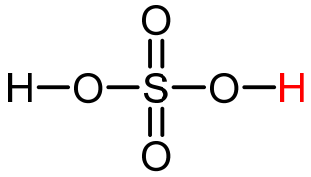
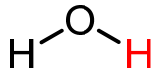
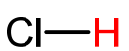
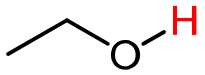
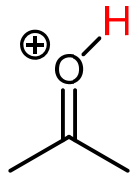
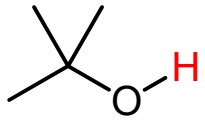
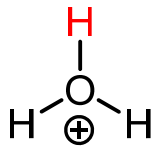
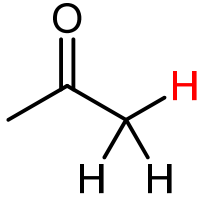
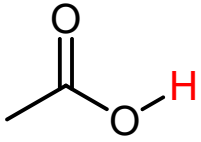
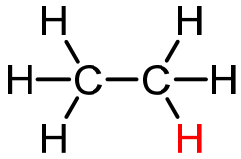
- Have an atom with a lone pair of electrons that can bond to H^+
- Nitrogen-containing compounds derived from ammonia are the most common organic bases
- Oxygen-containing compounds can react as bases when with a strong acid or as acids with strong bases



Some organic bases

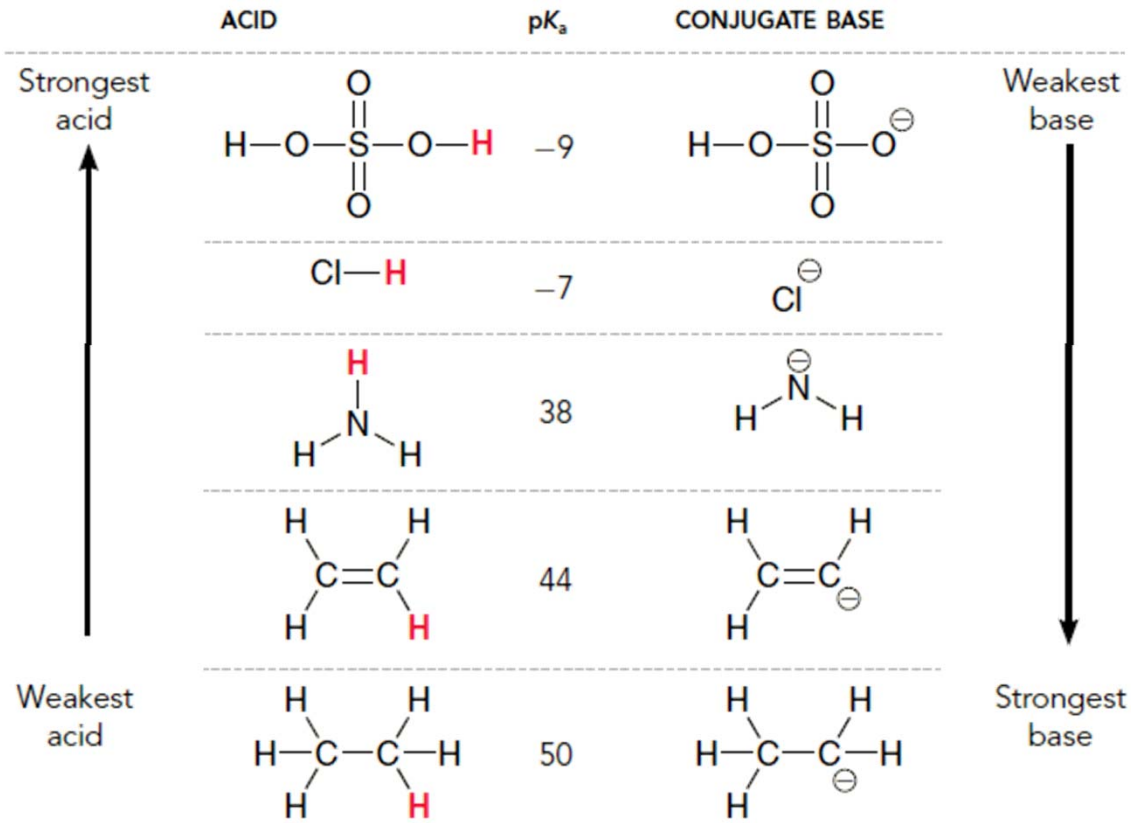
Methylamine Methanol Acetone

Quantifying Acidity and Basicity – Acidity

ACID	pK_a	ACID	pK_a
	–9		15.7
	–7		16
	–2.9		18
	–1.74		19.2
	4.75		50

- There are more acids and pK_a values in Table 3.1.
- Each pK_a unit represents an order of magnitude or a power of 10.
  - Which is stronger, HCl or H_2SO_4, and by exactly HOW MUCH?

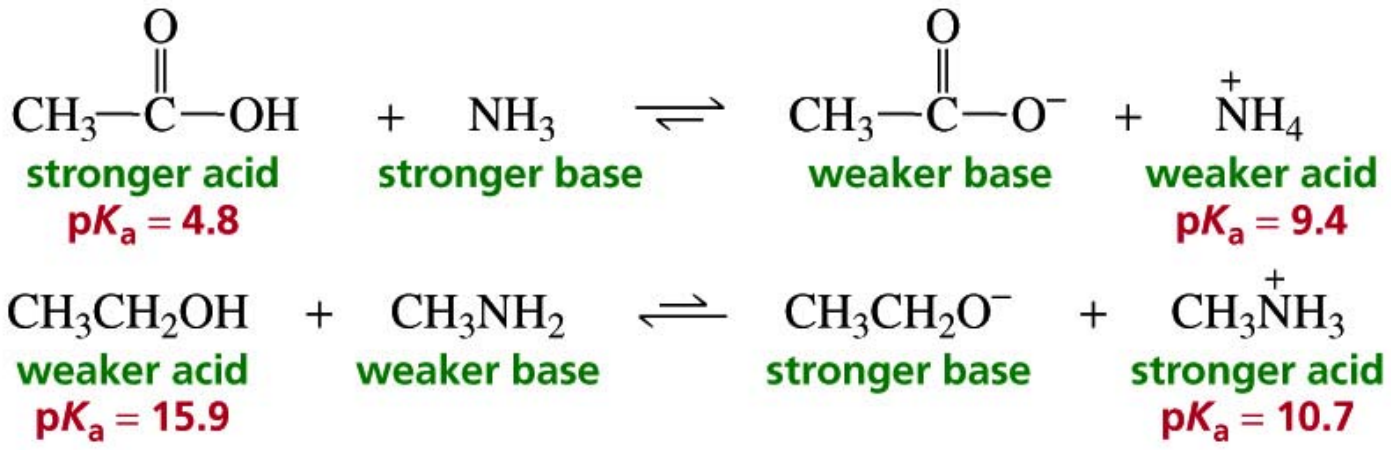
Quantifying Acidity and Basicity – Basicity



- You can also use pK_a values to compare the strengths of bases:
  - The stronger the acid the weaker its conjugate base. WHY?

Acids and Bases: pH and pKa

- Strong reacts to give weak.
- The stronger the acid, the weaker its conjugate base.
- Stable bases are weak bases.
- For an Acid-Base Reaction, the equilibrium lies toward the acid with the higher pKa, the predominant species at equilibrium.



Qualifying Acidity

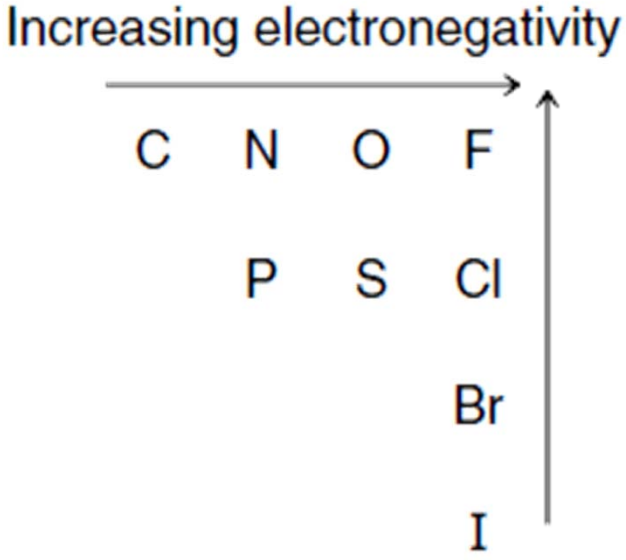
- The more effectively a conjugate base can stabilize its negative charge, the stronger the acid.
- What factors affect the stability of a negative formal charge?
  - The type of **atom** that carries the charge
  - **Resonance**
  - **Induction**
  - The type of **orbital** where the charge resides
- These factors can be remembered with the acronym, **ARIO**.

Qualifying Acidity – The Type of Atom

- **A**RIO—The type of **atom** that carries the charge:
  - More electronegative atoms are better at stabilizing negative charge. WHY?
  - Compare the acidity of the two compounds below:

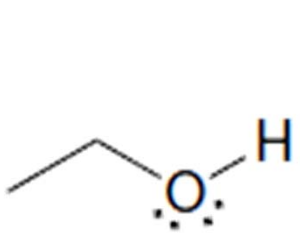
Butane

Propanol

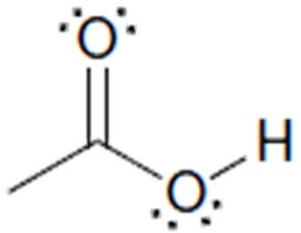


Qualifying Acidity – Resonance

- A**R**IO—**Resonance** can greatly stabilize a formal negative charge by spreading it out into partial charges.
- Compare the acidity of the two compounds below by comparing the stabilities of their conjugate bases. How does resonance play a role?



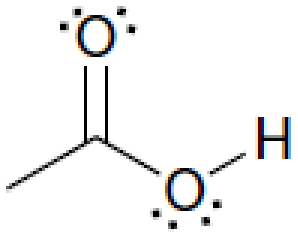
Ethanol



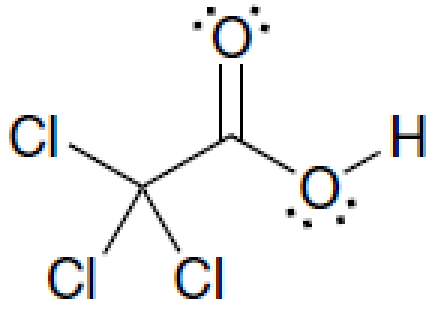
Acetic acid

Qualifying Acidity – Induction

- AR**I**O—**Induction** can also stabilize a formal negative charge by spreading it out. How is induction different from resonance?
- Compare the acidity of the two compounds below by comparing the stabilities of their conjugate bases. How does induction play a role?



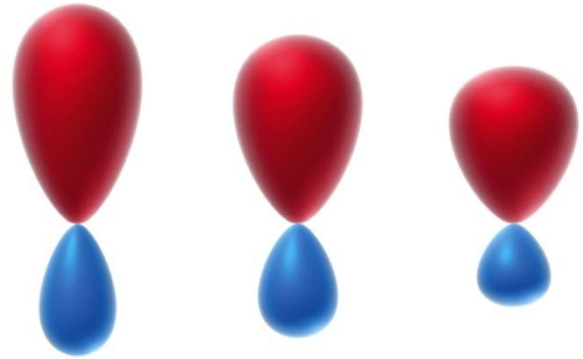
Acetic acid



Trichloroacetic acid

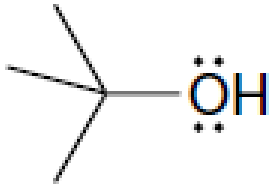
Qualifying Acidity – Orbital

- ARI**O** —The type of **orbital** also can affect the stability of a formal negative charge.
- Is a negative charge more stable or less stable if it is held closely to an atom's nucleus? WHY?
- Rank the ability of these orbitals (2s, 2p, sp^3, sp^2, and sp) to stabilize electrons, and explain.

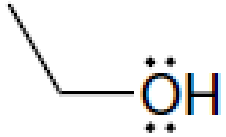


Solvation

- Because they are so similar, **it is difficult** to explain the pK_a difference between ethanol and *tert*-butanol.



tert-Butanol
$pK_a = 18$

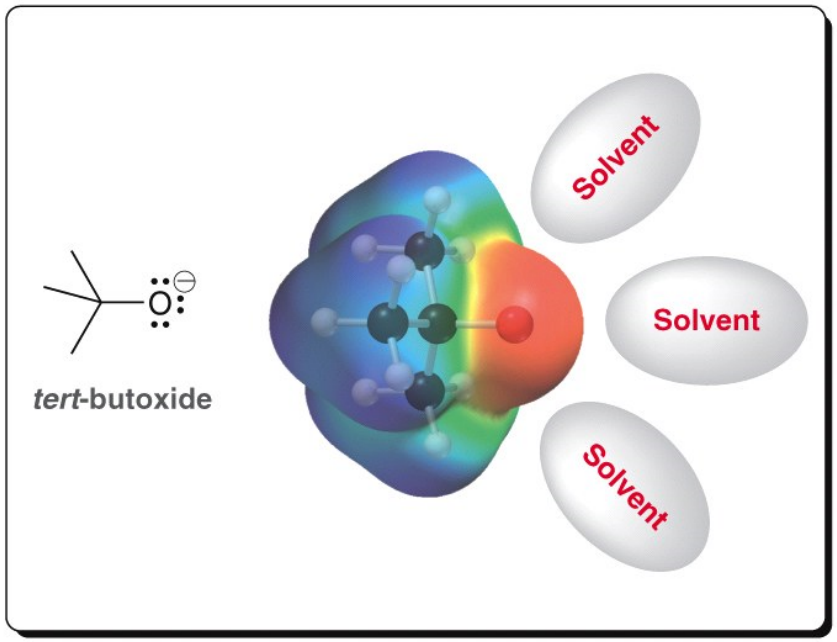


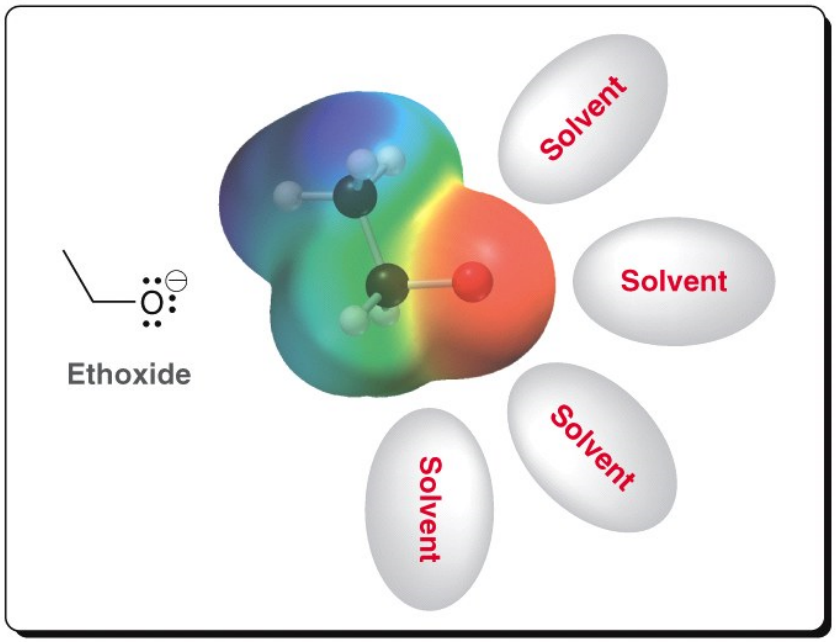
Ethanol
$pK_a = 16$

- Considering that pK_a values are measured in solution, how might the solvent act to make ethanol a slightly stronger acid? Think about how the solvent could stabilize its conjugate base.

Solvation

- The solvent must form ion–dipole attractions to stabilize the formal negative charge.
- If the *tert*-butoxide is sterically hindered, it won't be as well solvated as the ethoxide.





For Next Time….

- Friday Start Chapter 4 (4.1 – 4.5)
  - BRING YOUR MODEL SET!
- Homework Problems Chapter 3
  #1,4,7,15,34,35,37,39,43,44, 47
- Homework Problems Chapter 4
  #1, 6, 10, 19, 25, 28, 36, 43, 48, 51,52, 63