

Acid/Base Theories:

(1) Bronsted-Lowry

- Acid: proton (H^+) donor ----> conjugate base (species left after H^+ is lost)
- Base: proton acceptor ----> conjugate acid (species left after H^+ is gained)

*Still means any compound with a lone pair can be a base

Acidity: measure of a compound to give up a proton

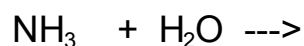
Basicity: measure of a compound's affinity for a proton

examples: Predict these reactions and ID A, B, CA, CB



Note:

Strong acids have weak CB

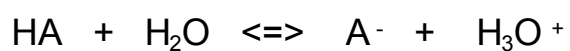


Strong bases have weak CA

What did water just do and why?

What is the conjugate base of CH_3COOH ?

2) Acid/Base Strength:



$$K_{\text{eq}} =$$

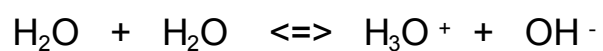
Formulas:

$$\text{pK}_a = -\log (\text{K}_a)$$

$$\text{K}_a = 10^{-\text{pK}_a}$$

- * The greater the pK_a , the weaker the acid
- * The greater the K_a , the stronger the acid
- * The stronger the acid, the weaker is its conjugate base.
- * For a reaction to take place, a stronger acid must go to a weaker acid and a stronger base must go to a weaker base
(H^+ will always go from the stronger acid to the stronger base)

For Water:



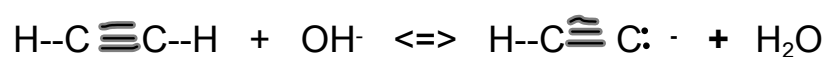
$$K_{\text{eq}} =$$

A strong acid is one that loses an H^+ easily, meaning that its conjugate base holds on to the H^+ weakly and is therefore a weak base

A weak acid is one that loses an H^+ with difficulty, meaning that its conjugate base holds on to the H^+ strongly and is therefore a strong base

EXAMPLES :

- 1) Water has a $pK_a = 15.74$, and acetylene has a $pK_a = 25$. Which of the two is more acidic? Will the hydroxide ion react with acetylene?



- 2) Butanoic acid, the substance responsible for the odor of rancid butter, has a $pK_a = 4.82$. What is its K_a ?

3) Formic acid, HCO_2H , has a $\text{pK}_a = 3.75$, and picric acid, $\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, has a $\text{pK}_a = 0.38$.

- a) What is the K_a of each?
- b) Which acid is stronger?

4) Is either of the following reactions likely to take place according to the pK_a data? ($\text{pK}_a \text{ HCN} = 9.31$; $\text{pK}_a \text{ ethanol} = 16$; $\text{pK}_a \text{ acetic acid} = 4.76$)

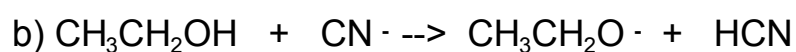
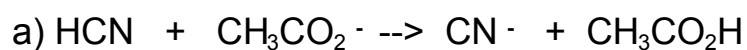


TABLE:

very strong acids	$\text{pK}_a < 1$
moderately strong acid	$\text{pK}_a = 1-3$
weak acids	$\text{pK}_a = 3-5$
very weak acids	$\text{pK}_a = 5-15$
extremely weak acids	$\text{pK}_a > 15$

Organic Acids and Bases:

Main Kinds of organic acids:

(1) Alcohols: H bonded to an electronegative Oxygen

ex: alcohols -OH methanol, $pK_a = 15.54$

(2) Carboxylic Acids: OH group bonded to a C=O

ex: acetic acid ($pK_a = 4.76$)

ex: formic acid ($pK_a = 3.75$)

(3) Amines: Compound with an NH_2 group

Each of these acids can also act as bases. Below are the two behavior reactions of acid and base:

Alcohol

Carboxylic acid

Amine

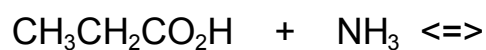
Organic Bases:

- characterized by the presence of an atom with a lone pair of electrons that can bond to H⁺ (reddish in the electrostatic potential map)
- nitrogen-containing compounds such as trimethylamine are the most common organic bases, but oxygen-containing compounds can also act as bases when reacting with a sufficiently strong acid
- amines are much more likely to act as bases, so we usually talk about the strength of its conjugate acid (pK_a)

Predicting Acid/Base reactions:

- 1) Find the most acidic proton of each acid
- 2) Estimate the pKa value based on known values
- 3) The direction of equilibrium shifts in the direction of the weaker acid (the one with the higher pKa value)

* Note: the shift will be quantitative (complete) if Δ pKa of acid/conj. acid is **> 3**

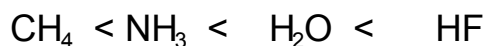


Stability:

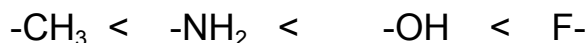
- stable bases are weak bases - they don't share their electrons well
- the weaker the base, the stronger is its conjugate acid
- the more stable the base, the stronger is its conjugate acid
- the more stable the base, the weaker it is
- dependent on 2 factors, electronegativity and size of atom

1) electronegativity

2nd row: $C < N < O < F$ with respect to electronegativity
they are similar in size



stability of their conjugate bases



Most electronegative wanting to hold on the electrons - most stable

The more electronegative the atom, the better it can bear its negative charge

2) Size:

- size is more important than electronegativity
- the strongest acid will be attached to the largest atom.
- with respect to size: $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$
- as the halide ion increases in size, its stability increases because its negative charge is spread over a larger volume of space. Its electron density decreases.

Weak Acids that might be encountered:



increase acidity --->

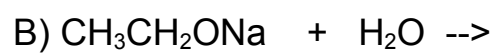
Their conjugate bases:

<---- increase basicity

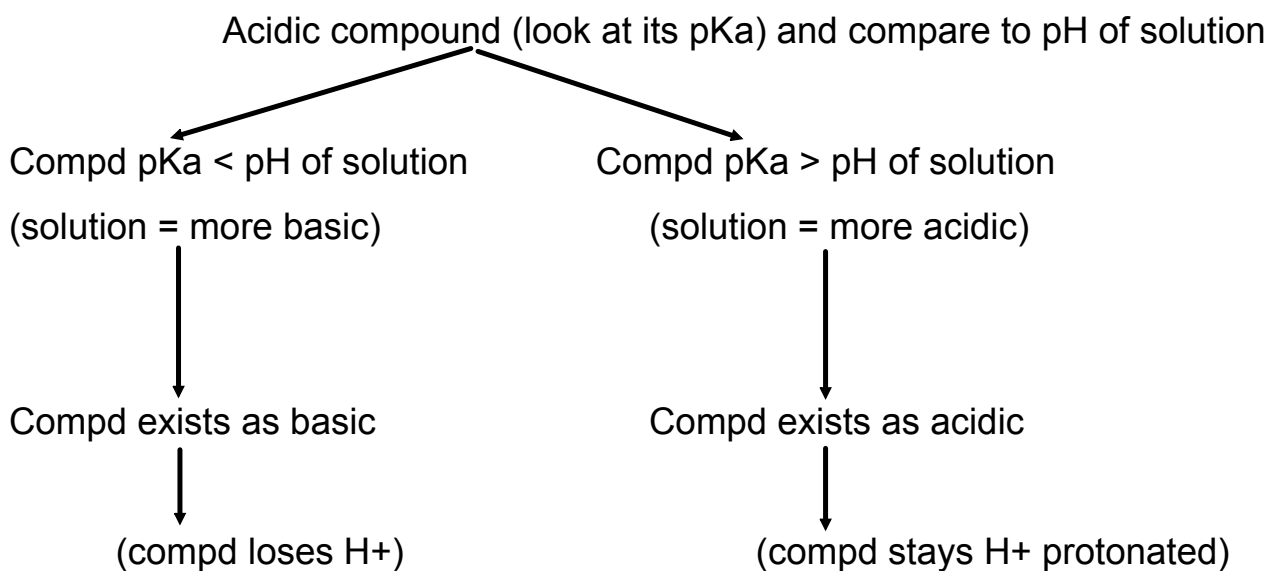
ex. Write a net ionic reaction that takes place when sodium hydride, NaH, is dissolved in ethyl alcohol

examples:

Write a net ionic equation for:



Determining structure of an acidic compound when placed in different pH's"



**If pH of solution = pKa of compound, the compound has = concentrations of its acidic and basic form.

What form will dominate in a solution with a pH = 5.5 ?

Ex. 1: $\text{CH}_3\text{CH}_2\text{OH}$ $\text{pK}_a = 15.9$

Ex. 2: $\text{CH}_3\text{CH}_2\text{OH}_2^+$ $\text{pK}_a = -2.5$

Ex. 3: CH_3NH_3^+ $\text{pK}_a = 11.0$

Buffer solutions:

- Solution with a weak acid and its CB
- Causes system to remain at a constant pH if small amts of acid or base are added

How does blood function as a buffer? - pg 43 blue box

Acidosis-

Alkalosis-

Lewis Acids/Bases:

Lewis Acid: - electron pair acceptor

Lewis Base: - electron pair donor

Our text: Acid: proton - donating acid

Lewis Acid: -non-proton-donating acid such as AlCl_3 or BH_3

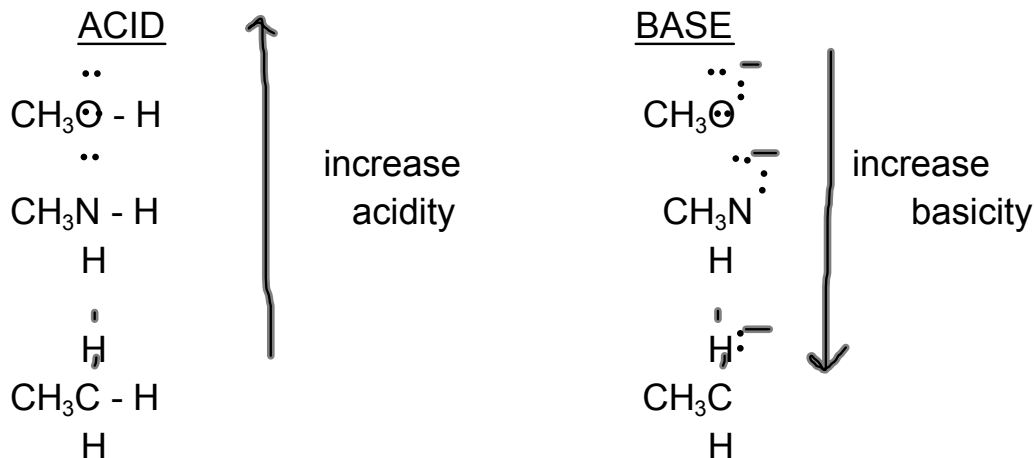
<u>From Appendix II:</u>	<u>pKa</u>
Binary strong acids	-10 to -7
Protonated carbonyl group	-8 to 0
Mineral acids (ternary acids)	-5 to 0
Carboxylic acids	0 to 5
Protonated nitrogen ions (aromatic)	1 to 5
Phenols	7 to 10
Protonated nitrogen ions (cyclic, alkyl)	10 to 12
alcohols, water	15
alkynes	25
alkenes	44

Molecular Structure and Acidity:

Ways to stabilize anions having a negative charge:

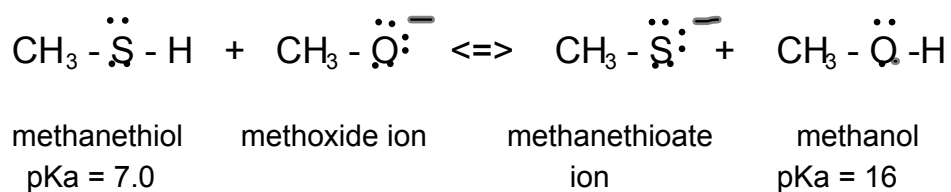
- A) on a more electronegative atom
- B) on a larger atom
- C) delocalized by the inductive effect
- D) in an orbital with more character
- E) delocalized through resonance

A) Atoms of similar size but a difference in electronegativity



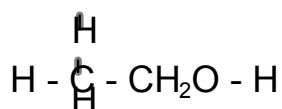
The greater the electronegativity of the atom bearing the negative charge the more stable the anion and the stronger the acid / the weaker the base

B) Size of the atom bearing the negative charge
- the larger the atom bearing the negative charge, the greater its stability

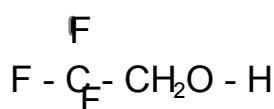


C) Electron -withdrawing inductive effect

- the polarization of electron density of a covalent bond due to the electronegativity of an adjacent covalent bond
- the shifting of electrons in a sigma bond in response to the electronegativity of nearby atoms
- the withdrawal or donation of electrons in a sigma bond due to electronegativity

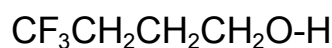
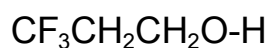
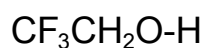


pka = 15.9



pKa = 12.4

- stabilization by the inductive effect falls off rapidly with the increasing distance of the electronegative atom from the site of negative charge



D) Hybridization

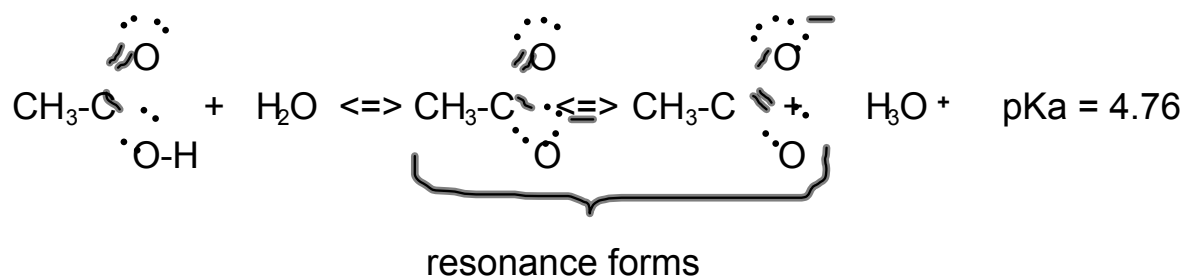
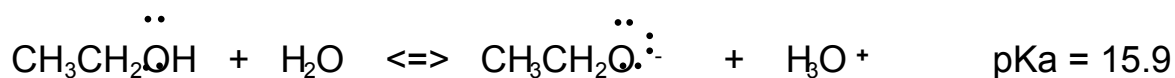
- the greater the % s character to the hybrid orbital of the charged atom, the more stable the anion
- consider the acidity of alkanes, alkenes, and alkynes (given for comparison are the acidities of water and ammonia)

	<u>weak acid</u>	<u>conjugate base</u>	<u>pKa</u>
	water	HO -	15.7
	alkyne	HC \equiv C -	25
	ammonia	H ₂ N -	38
	alkene	H ₂ C=CH -	44
	alkane	CH ₃ CH ₂ -	51

increase
acidity

E) resonance delocalization of charge in A⁻

- the more stable the anion, the farther the position of equilibrium is shifted to the right
- compare the acidity alcohols and carboxylic acid



- carboxylic acids are stronger acids than alcohols as a result of the resonance stabilization

