## *Acid-Base Chemistry*

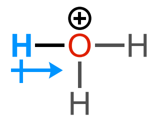
This page describes the common definitions of acids and bases that you will encounter, in short, the terms "acid" and "base" describe the movement of protons ($H^+$) whereas the terms "nucleophile" and "electrophile" describe the movement of **electrons**

### *Brønsted Definition*

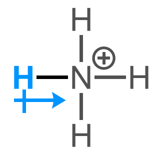
***Acid**: proton donor,* **H—A**

***proton** - **H**$^{\oplus}$*

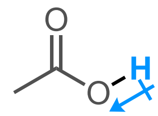
examples:



$H_3O^{\oplus}$



$NH_4^{\oplus}$



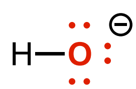
$CH_3COOH$

**Note**: that although the formal positive charge may be drawn on the heteroatom, the bond dipole correctly indicates that the **proton** bears the positive charge.

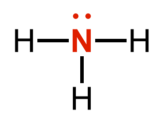
***Base**: proton acceptor,* **B:**

**i.e.** electron pairs (lone pairs or π electrons) are bases

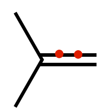
examples:



$^{\ominus}OH$



$NH_3$



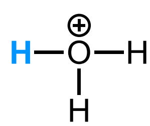
*π-electrons*

### *Lewis Definition*

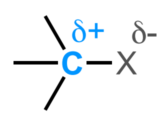
**Electrophile (Lewis acid):** electron acceptor

**i.e.** Bronsted acids (**H**$^{\oplus}$) **and** atoms w/ partial postive charge or empty p-orbitals

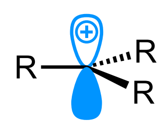
examples:



$H^{\oplus}$



*alkyl halide*

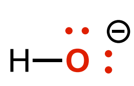


*carbocation*

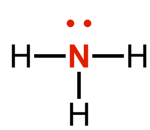
**Nucleophile (Lewis base):** electron donor

**i.e.** electron pairs (lone pairs or π electrons) are bases — same as the Bronsted examples

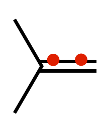
*examples:*



$^{\ominus}OH$



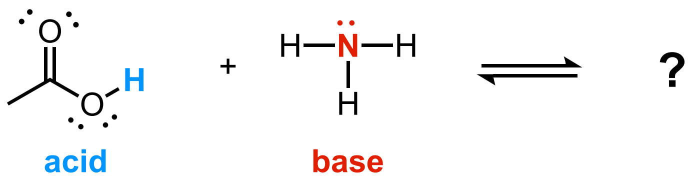
$NH_3$



*π-electrons*

## *Predicting Acid-Base Reactions*

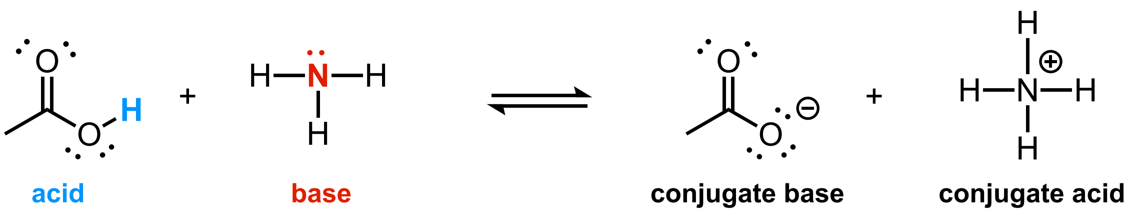
Using the reaction shown below, this page describes the stepwise thought process for determining the products and extent of an acid-base reaction, as well as the reaction mechanism




**1) Draw products of an acid-base reaction** (conjugate acid and conjugate base)

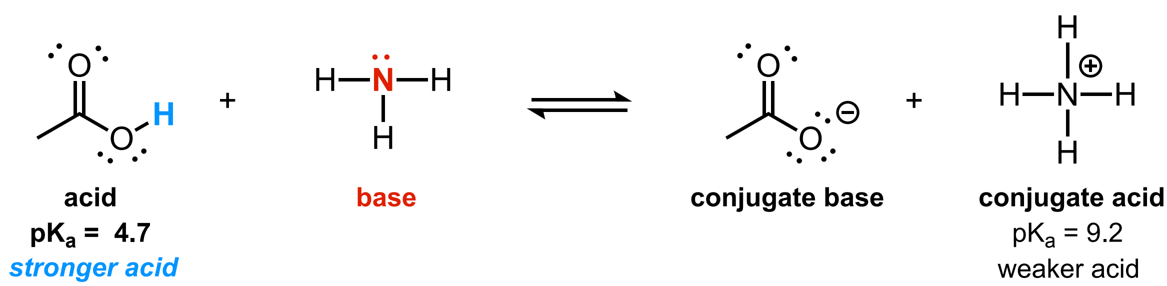
***Conjugate Acid:*** *the product of the base accepting* $H^{\oplus}$

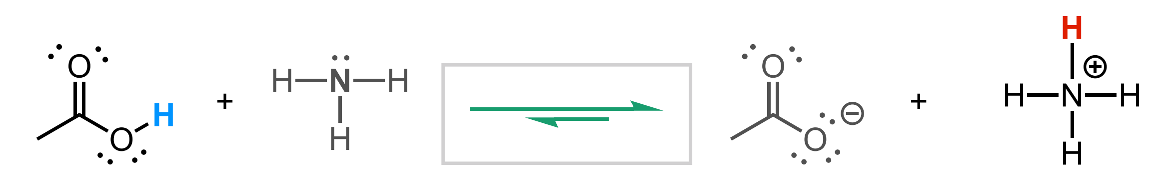
***Conjugate Base:*** *the product of the acid donating* $H^{\oplus}$




**2) Compare pKas of the acid** (reactant side) **and conjugate acid** (product side)**.**

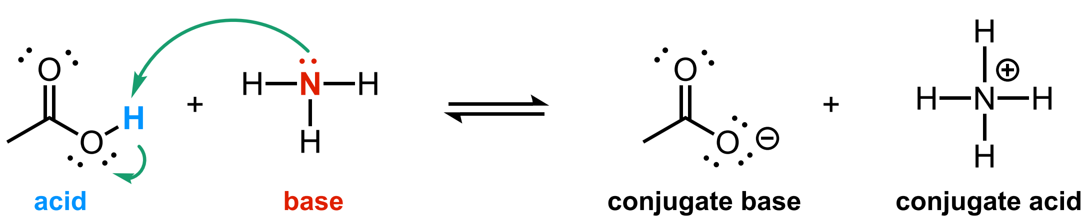
Remember that stronger acids have <u>*lower*</u> $pK_a$s.



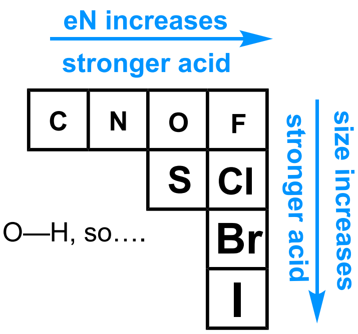

**The stronger acid *wants to donate* its proton**, therefore the equilibrium favors the formation of the weaker conjugate acid

**3) Use the Lewis definition to illustrate the <u>*mechanism*</u> of the reaction.**



## *Predicting relative acid strength without $pK_a$ values*

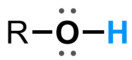
While a $pK_a$ table is more conclusive, it is possible to predict relative acidities simply based upon molecular structure. In order to do this, four structural characteristics must be analyzed (in this order)



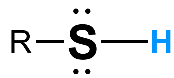

### 1) **Atom: Periodic Trends**

**For atoms in the same group/column**, larger atoms have longer (weaker) bonds to H and are stronger acids

example:



alcohol
~ 17



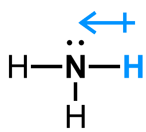
thiol
~10
**stronger acid**

**$pK_a$**

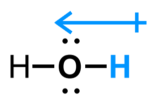
S—H is a longer bond than O—H, so….
S—H is a weaker bond
S—H is a stronger acid

**For atoms in the same period/row**, more electronegative (eN) atoms induce larger partial positive charges on H and are stronger acids

example:



ammonia
36



water
14
**stronger acid**

**$pK_a$**

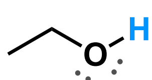
O—H is more polar than N—H, so…
O—H has a larger $\delta^+$ on H
O—H is a stronger acid

### 2) Resonance: Stabilized Conjugate Bases

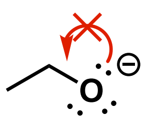
Conjugate bases that are stabilized (for example, through resonance) correlate with stronger acids

**acid**
**$pK_a$**

ethanol
17



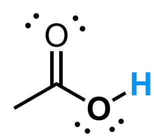
**conjugate base**

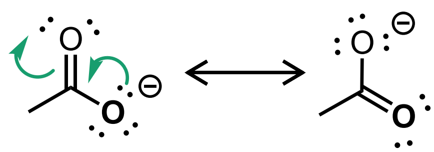


no resonance in ethoxide

**acid**
**$pK_a$**

acetic acid
**4.7**
***stronger acid***



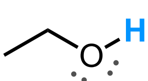


resonance delocalization of negative charge on O stabilizes the conjugate base

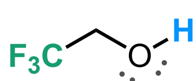
### 3) Inductive Effects: Electron Withdrawing Effects

Electron-withdrawing groups (EWGs, e.g. halide) in proximity to a proton results in a stronger acid

example:

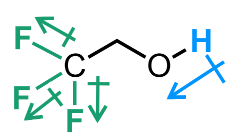


ethanol
17




trifluoroethanol
11.3
**stronger acid**

**$pK_a$**

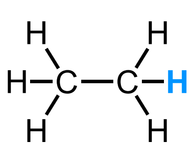


C—F bond dipoles "pull" electron density away from O—**H**, increasing $\delta^+$ on **H**

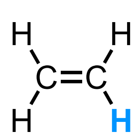
### 4) Hybridization of C atom: Molecule <u>only</u> contains C-H

Hybridization of C ("s-character") stabilizes conjugate base (carbanion)

*example:*



ethane
62



ethylene
45

H−C≡C−**H**

acetylene
**26 (stronger acid)**

**$pK_a$**


**$sp^3$ $sp^2$ sp**