Acidez e Basicidade

A substância pode ser classificada como um **ácido** or uma **base**.

A palavra **ácido** vem do Latim ***acere*** que significa azedo. Uma **base** é um **álcali**, a qual é derivada da palavra árabe ***al-quali***.

A presença de ácidos e bases é reconhecida desde a antiquidade.

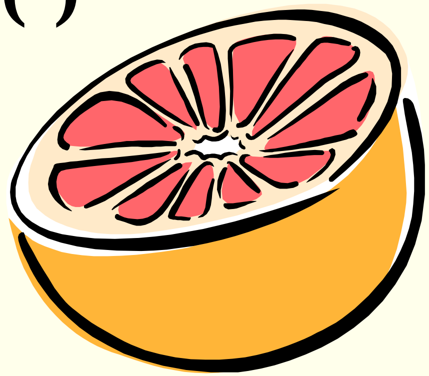
Lavoisier propôs que o oxigênio seria o elemento dos quais os ácidos seriam originados.

Liebig (Alemanha) propôs que um ácido contém hidrogênio.

Muitas reações químicas são classificadas como **reações ácido-base**; não são necessariamente neutralizações.

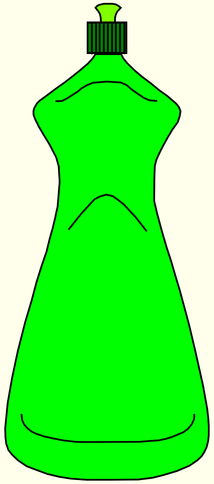
Ácidos

- Produzem íons H^+ (como H_3O^+) em água
- Produzem também um íon negativo (-)
- Sabor azedo
- Corroem metais
- Reagem com bases formando sais e água



Bases

- Produzem íons OH^- em água
- Taste amargo, adstringente
- São eletrólitos
- Textura de sabão, escorregadios
- Reagem com ácidos para formar sais e água



Brønsted-Lowry Theory

- Brønsted and Lowry came up with an alternative definition for acids and bases

Brønsted-Lowry Theory

- In the Bronsted-Lowry definition:

An ***acid*** is a substance from which a proton can be removed (proton donor)

A ***base*** is a substance that can remove a proton from an acid (proton acceptor)

Bronsted-Lowry Concept

$$HCl + H_2O \Longrightarrow H_3O^+ + Cl^-$$

acid base

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

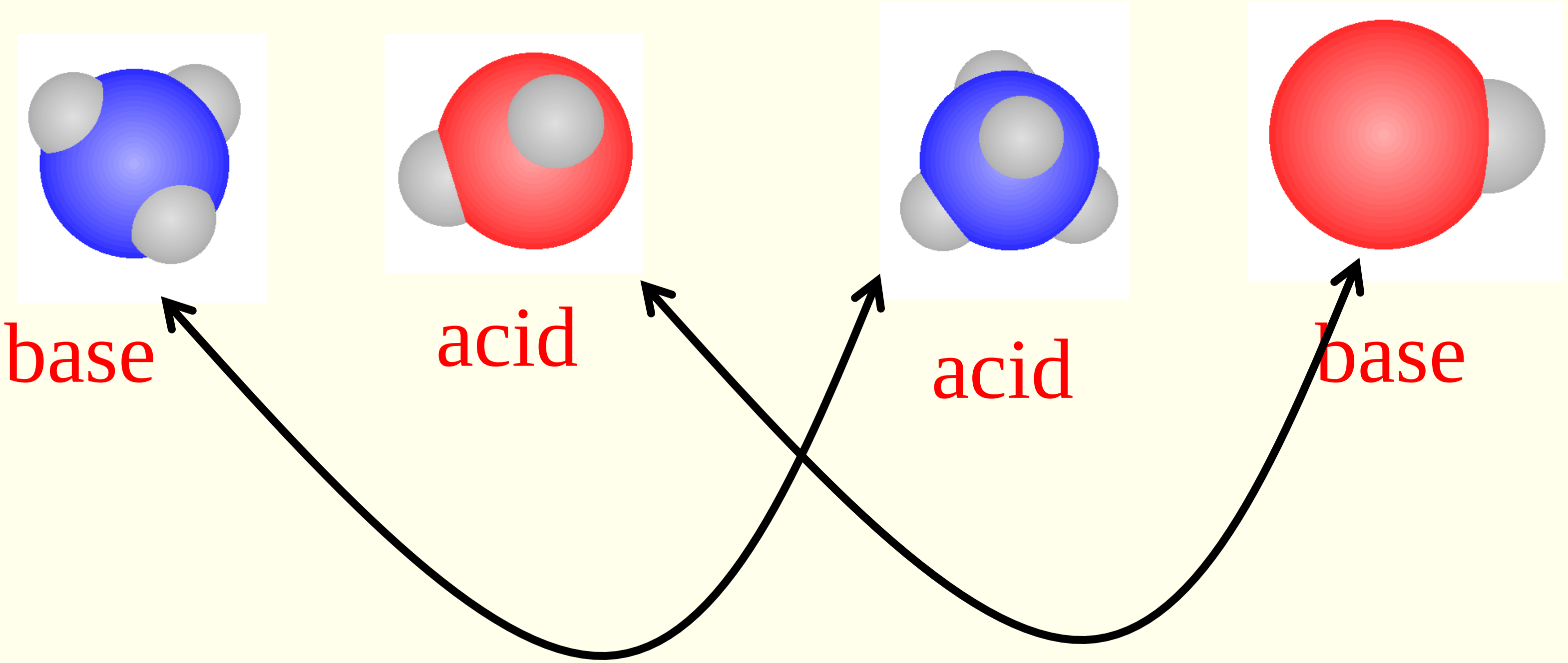
base acid

Brønsted-Lowry Concept

- Bronsted-Lowry Concept (J. Brønsted, T. Lowry, 1923)
  - Acid-base reaction involves proton transfer
  - Acid: proton donor
  - Base: proton acceptor
    - does not have to have OH^- in formula
  - Water is amphoteric
  - Acids & bases can be molecules or ions

Brønsted-Lowry Concept

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$



base

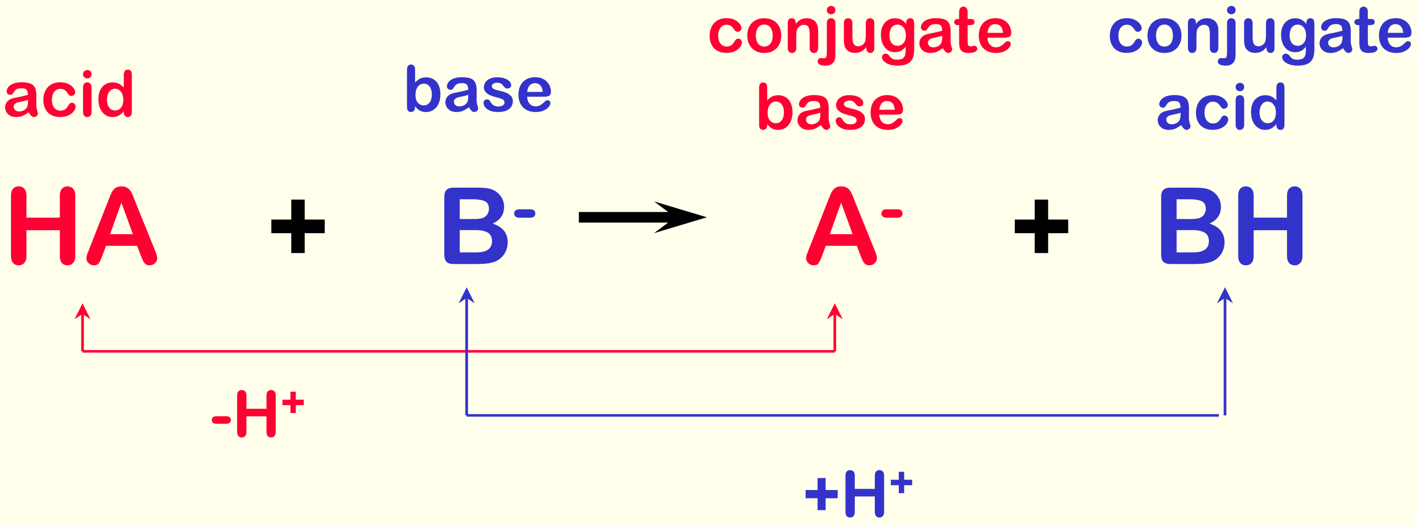
acid

acid

base

Acid-base conjugate pairs

Brønsted-Lowry Theory



acid base conjugate base conjugate acid

$$HA + B^{-} \longrightarrow A^{-} + BH$$

$-H^{+}$

$+H^{+}$

acid = proton donor

base = proton acceptor

Conjugate Acid = Base + Proton

Conjugate Base = Acid - Proton

Acid-Base Strength

- Strong acids
  - Ionize completely in water

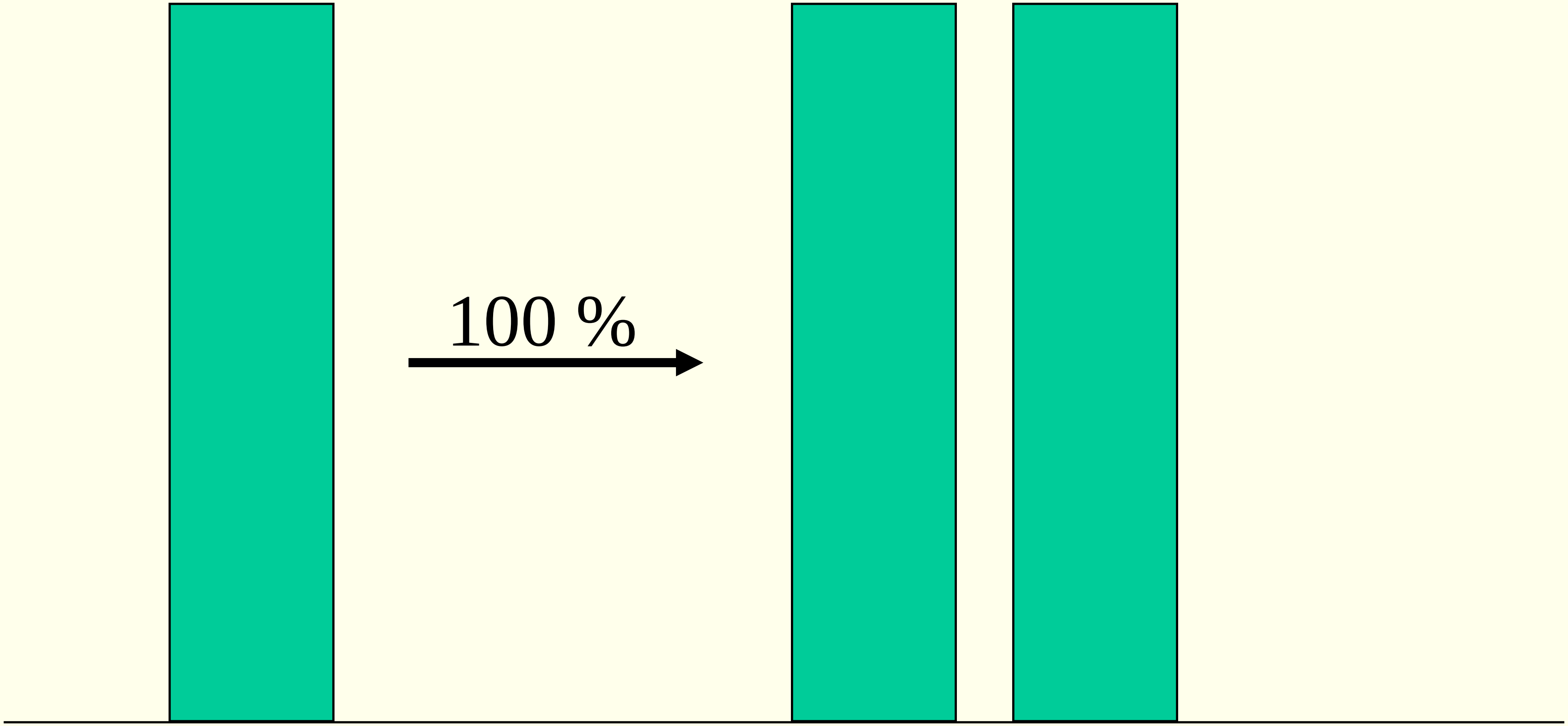
$$HX + H_2O \rightarrow H_3O^+ + X^-$$

- Weak acids
  - Ionize only partially in water

$$HX + H_2O \leftrightarrow H_3O^+ + X^-$$

  - Common weak acids: Numerous molecules and certain cations (we’ll learn more about these later)

Strong Acids



Before Equilibrium
HX

At Equilibrium
H_3O^+ X^-

100 %

Acid-Base Strength

- Common Strong Acids (Know these!)

  HCl

  HBr

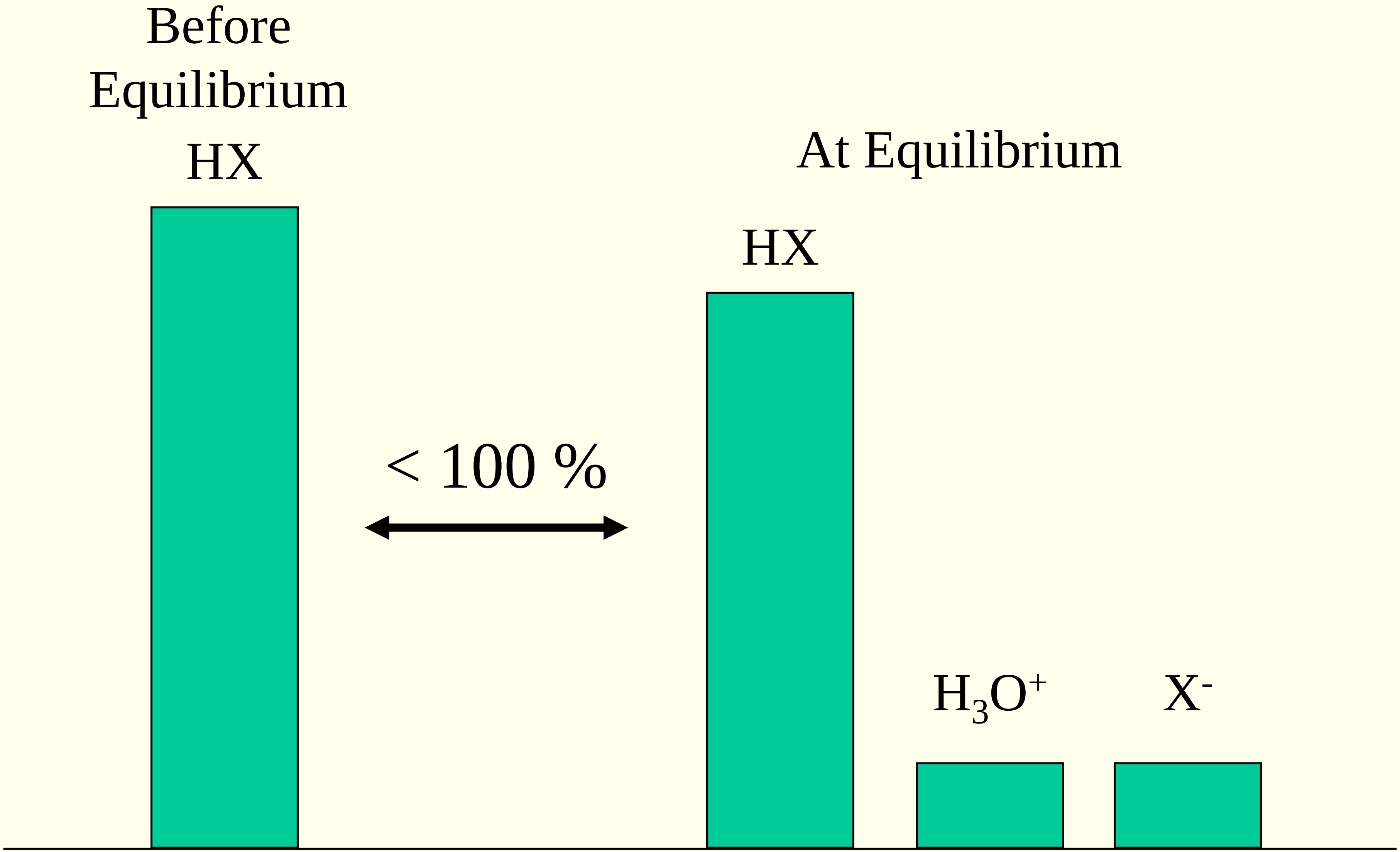
  HI

  HNO_3

  $HClO_4$

  H_2SO_4

Weak Acids



Before Equilibrium

HX

< 100 %

At Equilibrium

HX

H_3O^+

X^-

Acid-Base Strength

- Strong bases
  - Ionize completely in water

$$NaOH \rightarrow Na^+ + OH^-$$

  - Common strong bases: MOH and $M(OH)_2$, M_2O and MO (M = Grp IA and IIA metals)
- Weak bases
  - Ionize only partially in water

$$B + H_2O \leftrightarrow BH^+ + OH^-$$

  - Common weak bases: NR_3 (R = H or other chemical species) and certain anions

Relative Acid-Base Strength

Strongest	$HClO_4$	ClO_4^-	Weakest
Acids	H_2SO_4	HSO_4^-	Bases
	HCl	Cl^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
	HSO_4^-	SO_4^{2-}	
	HNO_2	NO_2^-	
	$HClO$	ClO^-	
Weakest	NH_4^+	NH_3	Strongest
Acids	H_2O	OH^-	Bases
	OH^-	O^{2-}	
	H_2	H^-	

Strongest acid that can exist in H_2O

Strongest base that can exist in H_2O

Autoionization of Water

- In pure water, the following equilibrium occurs: $H_2O_{(\ell)} + H_2O_{(\ell)} \leftrightarrow H_3O^+{}_{(aq.)} + OH^-{}_{(aq.)}$
- The equilibrium constant for this reaction is the ion product, K_w:

$$K_w = [H_3O^+][OH^-]$$

  - $[H_3O^+] = [OH^-] = 1 \text{ x } 10^{-7}$ mol/L (25 °C)

so

$$K_w = 1 \text{ x } 10^{-14} \text{ (25 °C)}$$

The pH scale

Sørensen introduced the pH scale in 1909 using the symbol p_H.
The *p* is from the German word *potenz,* power of (10).

$\mathbf{pH = -\log [H^+];}$ $\mathbf{[H^+] = 10^{-pH}}$
$\mathbf{pOH = -\log [OH^-];}$ $\mathbf{[OH^-] = 10^{-pOH}}$
$\mathbf{p\mathit{K} = -\log [\mathit{K}];}$ $\mathbf{\mathit{K} = 10^{-p\mathit{K}}}$

pH =	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$[H^+]$ =	0.79	0.63	0.50	0.40	0.32	0.25	0.20	0.16	0.13

(not linear; need not copy, figure out yourself)

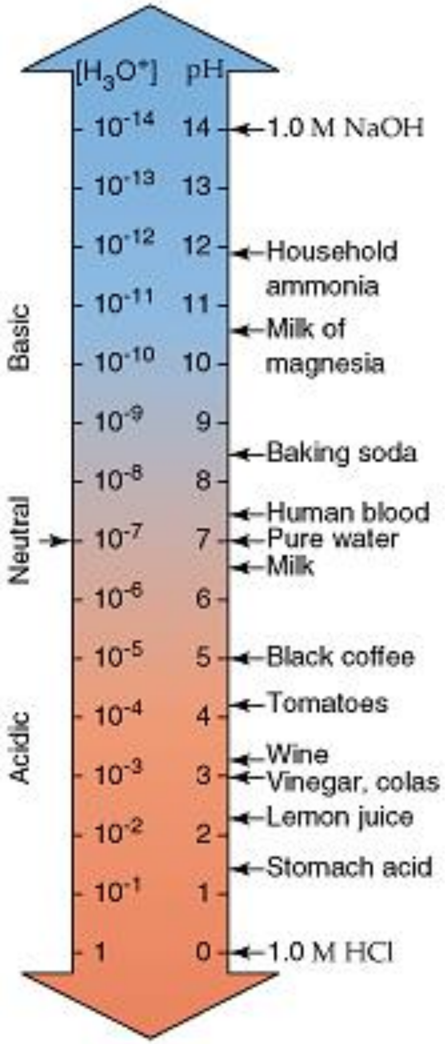
For aqueous solution;

$$K_w = [H^+]\,[OH^-]$$
$$-\log K_w = pH + pOH = 14 \text{ only at } 25^{o}C$$

pH meter and pH electrodes

The pH meter is based on the principle to be discussed in electrochemistry.

This topic is also related to the equilibrium constant *K* and Gibbs free energy, ΔG.


$[H_3O^+]$
pH
Basic
Neutral
Acidic
10^{-14} 14 1.0 M NaOH
10^{-13} 13
10^{-12} 12 Household ammonia
10^{-11} 11 Milk of magnesia
10^{-10} 10
10^{-9} 9 Baking soda
10^{-8} 8 Human blood
10^{-7} 7 Pure water
Milk
10^{-6} 6
10^{-5} 5 Black coffee
10^{-4} 4 Tomatoes
Wine
10^{-3} 3 Vinegar, colas
Lemon juice
10^{-2} 2 Stomach acid
10^{-1} 1
1 0 1.0 M HCl

Brønsted-Lowry definition

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

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

$$pK_a = -\log K_a$$

$K_a = 10^{-5}$ $pK_a =$

$K_a = 10^{-8}$ $pK_a =$

$$K_b(A^-) = \frac{K_w}{K_a(HA)} = \frac{[HA][OH^-]}{[A^-]}$$

e.g., CH_3CO_2H $K_a = 1.8 \times 10^{-5}$ $K_b = 5.6 \times 10^{-10}$ $CH_3CO_2^-$

$pK_a = 4.7$ $pK_b = 9.3$

HCN $K_a = 7.9 \times 10^{-10}$ $K_b = 1.3 \times 10^{-5}$ CN^-

$pK_a = 9.1$ $pK_b = 4.9$

pK_a

pK_a = - log K_a

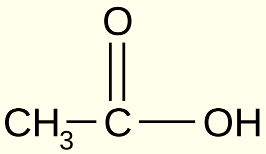
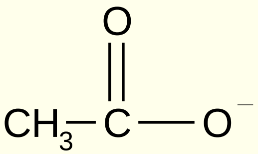
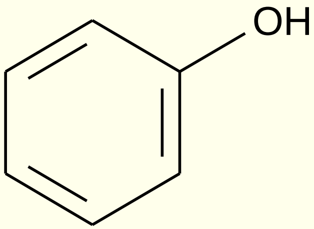
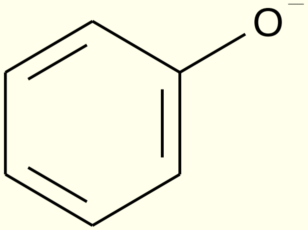
Strong acid = large K_a = small pK_a

Weak acid = small K_a = large pK_a

Relative Acid and Base Strengths

ACID STRENGTH: weaker → stronger

BASE STRENGTH: weaker → stronger

ACID	CONJ. BASE	K_a	pK_a
$HClO_4$	ClO_4^-	10^{10}	-10
 $CH_3-\overset{\overset{O}{\|}}{C}-OH$	 $CH_3-\overset{\overset{O}{\|}}{C}-O^-$	10^{-5}	5
		10^{-10}	10
$CH_3CH_2O\text{-}H$	$CH_3CH_2O^-$	10^{-16}	16
CH_3-CH_3	$CH_3-CH_2^-$	10^{-50}	50

Acid Strengths

Strong Acid

- Conjugate base is weak
- pK_a is small

Weak Acid

- Conjugate base is strong
- pK_a is large

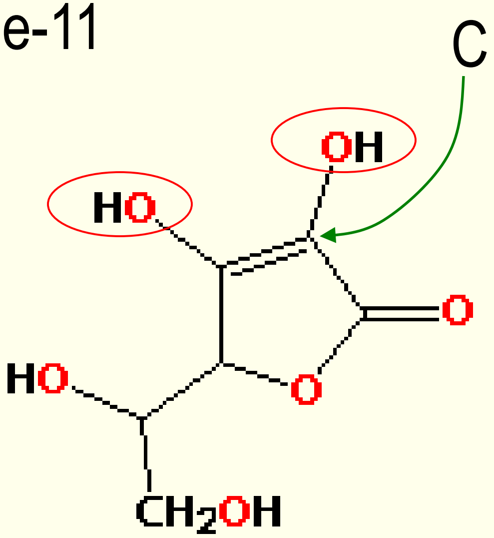
Polyprotic acids

Polyprotic acids such as sulfuric and carbonic acids have more than one hydrogen to donate.

$H_2SO_4 = H^+ + HSO_4^-$ K_{a1} very large completely ionized
$HSO_4^- = H^+ + SO_4^{2-}$ $K_{a2} = 0.012$

$H_2CO_3 = H^+ + HCO_3^-$ $K_{a1} = 4.3e\text{-}7$
$HCO_3^- = H^+ + CO_3^{2-}$ $K_{a2} = 4.8e\text{-}11$

Ascorbic acid (vitamin C) is a diprotic acid, abundant in citrus fruit.



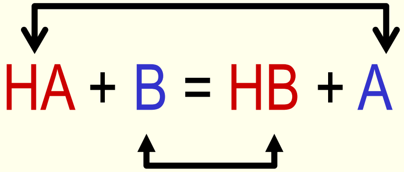
Others:
H_2S, H_2SO_3, H_3PO_4, $H_2C_2O_4$ (oxalic acid) …

Problems with B-L theory

The theory works very nicely in all protic solvent, but fails to explain acid-base behaviour in aprotic solvents and non-solvent situations.

A more general concept on acid and base was proposed by G.N. Lewis at about the same time Bronsted-Lowry theory was proposed.

Evolution of the acid-base concept

year	**thinker**	**Acid**	**Base**	**acid-base reaction**
1884	Arrhenius	ionize H^+	ionize OH^-	$H^+ + OH^- = HOH$
1923	Bronsted-	Proton	proton	 $HA + B = HB + A$
	Lowry	Donor	acceptor	conjugation
1923	Lewis	electrophil	nucleophil	$E + Nu = E{:}Nu$

1923 - G.N. Lewis

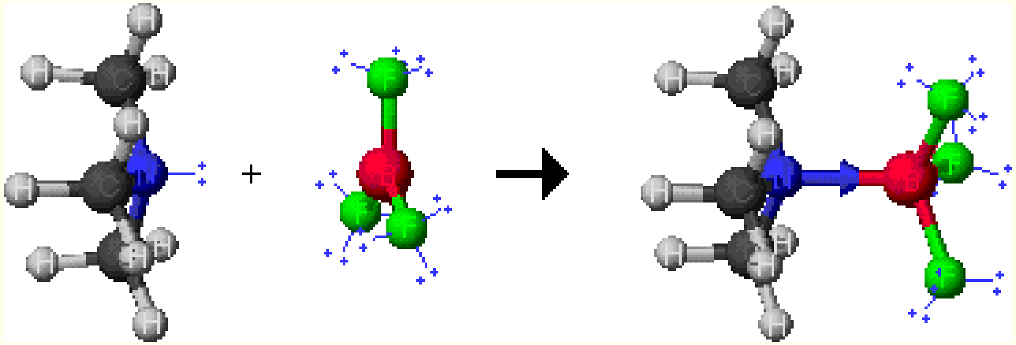
Proposed another method of defining acids and bases. **Lewis acid** - Any substance that can accept a pair of nonbonding electrons.

aka: **electron-pair acceptor**

Lewis base - Any substance that can donate a pair of nonbonding electrons.

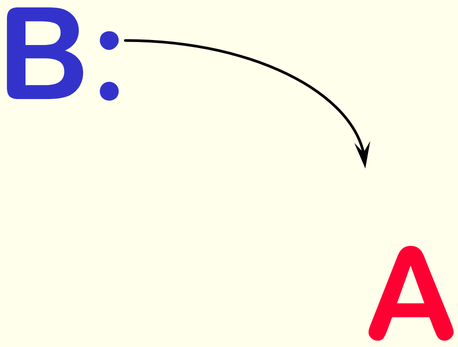
aka: **electron-pair donor**

BF3 + :NH3 → F3B:NH3



Lewis Acid-Base theory

more general than Bronsted theory



BASE

electron-pair donor

ACID

electron-pair acceptor

Some Lewis Acids: Fe^{3+} BF_3 H_3O+

Some Lewis Bases: NH_3 H_2O

Electronegativity and Size Effects

Sect. 7.5: Electronegativity and Size

increased electronegativity increases acidity

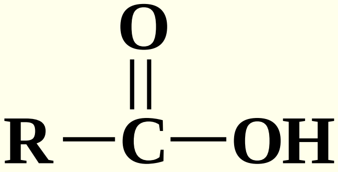
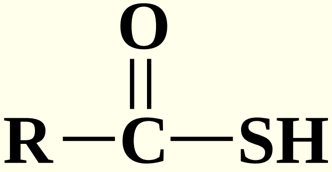
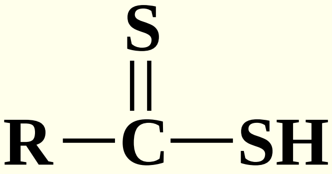
C	N	O	F
Si	P	S	Cl
		Se	Br
			I

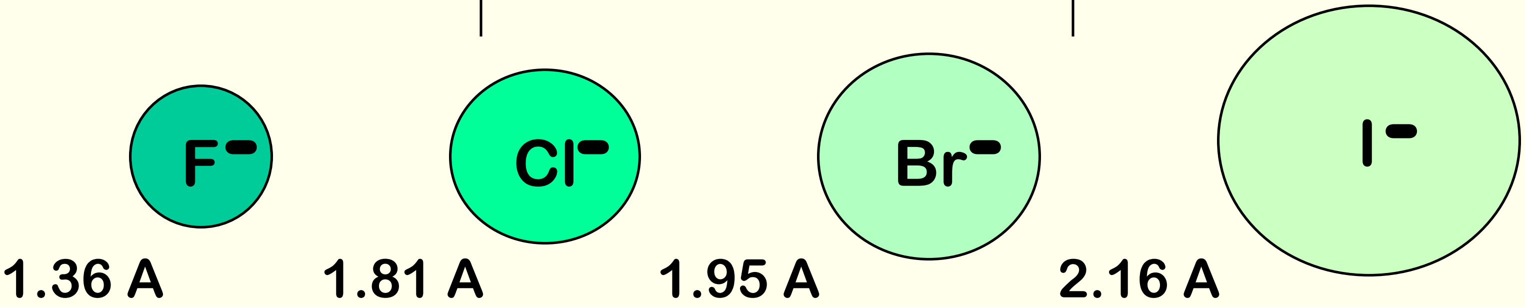
increased size increases acidity

Effect of Atomic Size on Acidity

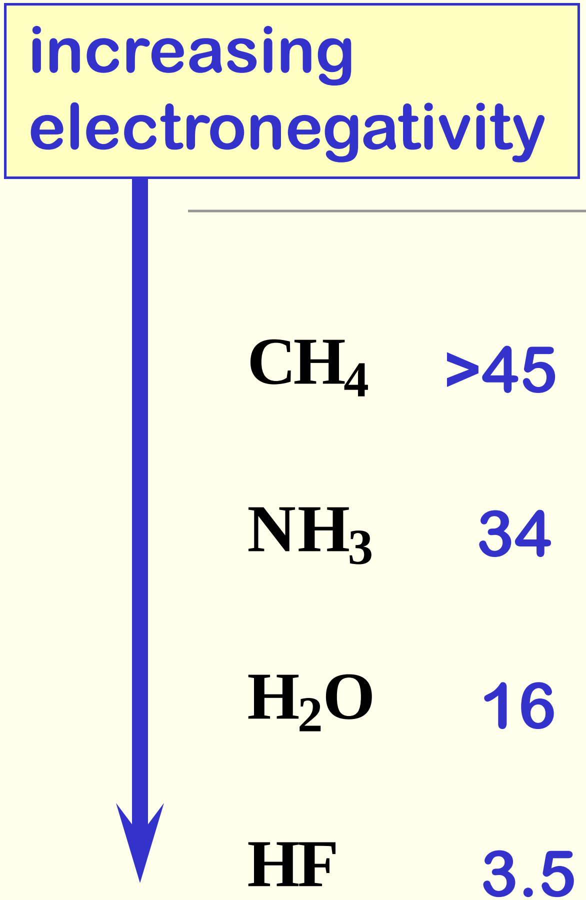
increasing
atom size

pKa Values

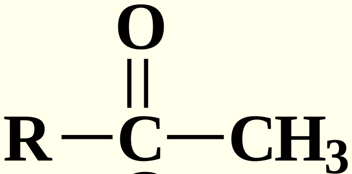
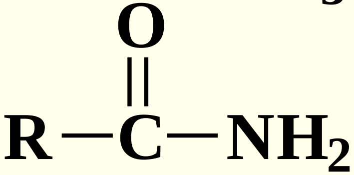
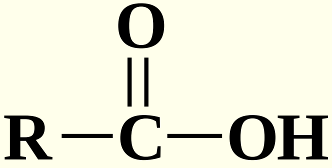
HF	3.5	HOH	16	 $R-\overset{\overset{O}{\|}}{C}-OH$	5
HCl	-7	HSH	7	 $R-\overset{\overset{O}{\|}}{C}-SH$	
HBr	-9	HSeH	4	 $R-\overset{\overset{S}{\|}}{C}-SH$	
HI	-10	HTeH	3		

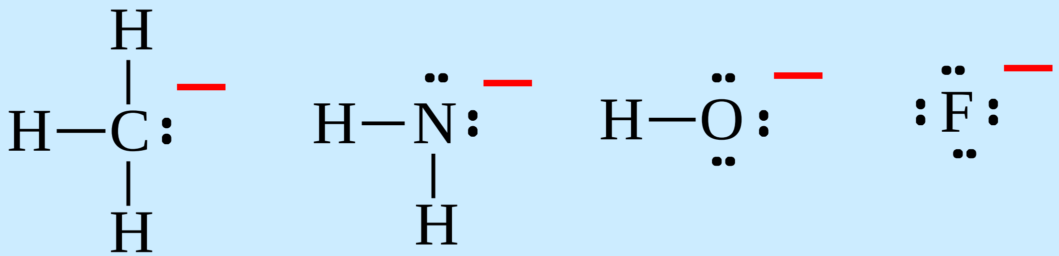


Effect of Electronegativity on Acidity



pKa Values

CH_4	>45	RCH_3	45	 $R-\overset{\overset{O}{\|}}{C}-CH_3$	20
NH_3	34	RNH_2	35	 $R-\overset{\overset{O}{\|}}{C}-NH_2$	15
H_2O	16	ROH	18	 $R-\overset{\overset{O}{\|}}{C}-OH$	5
HF	3.5				



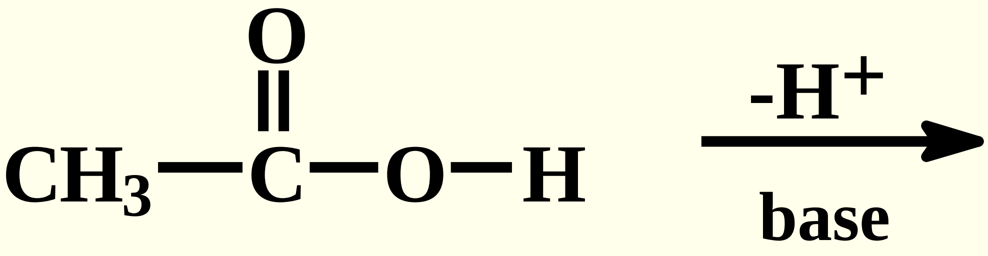
Resonance Effects

Take Away Lession:

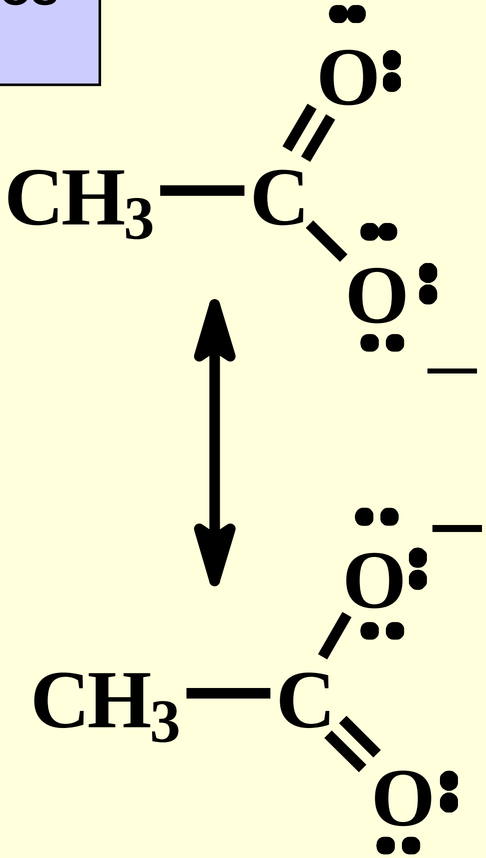
Resonance strengthens acid
Resonance weakens base

Resonance in the Acetate Ion

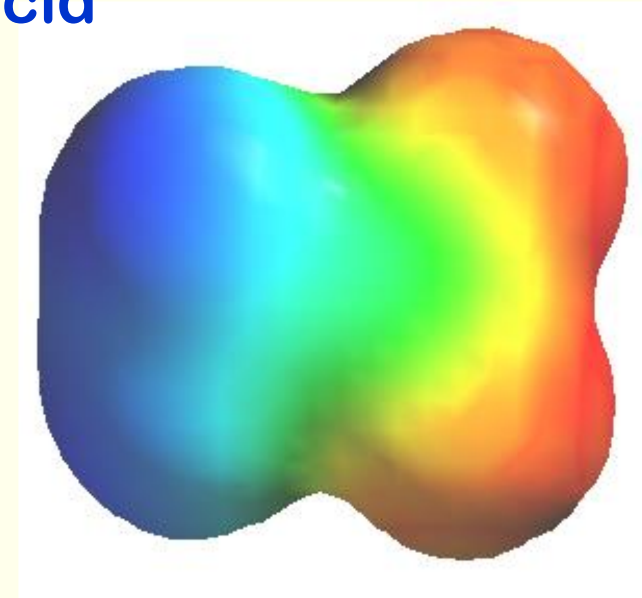
equivalent structures
charge on oxygens



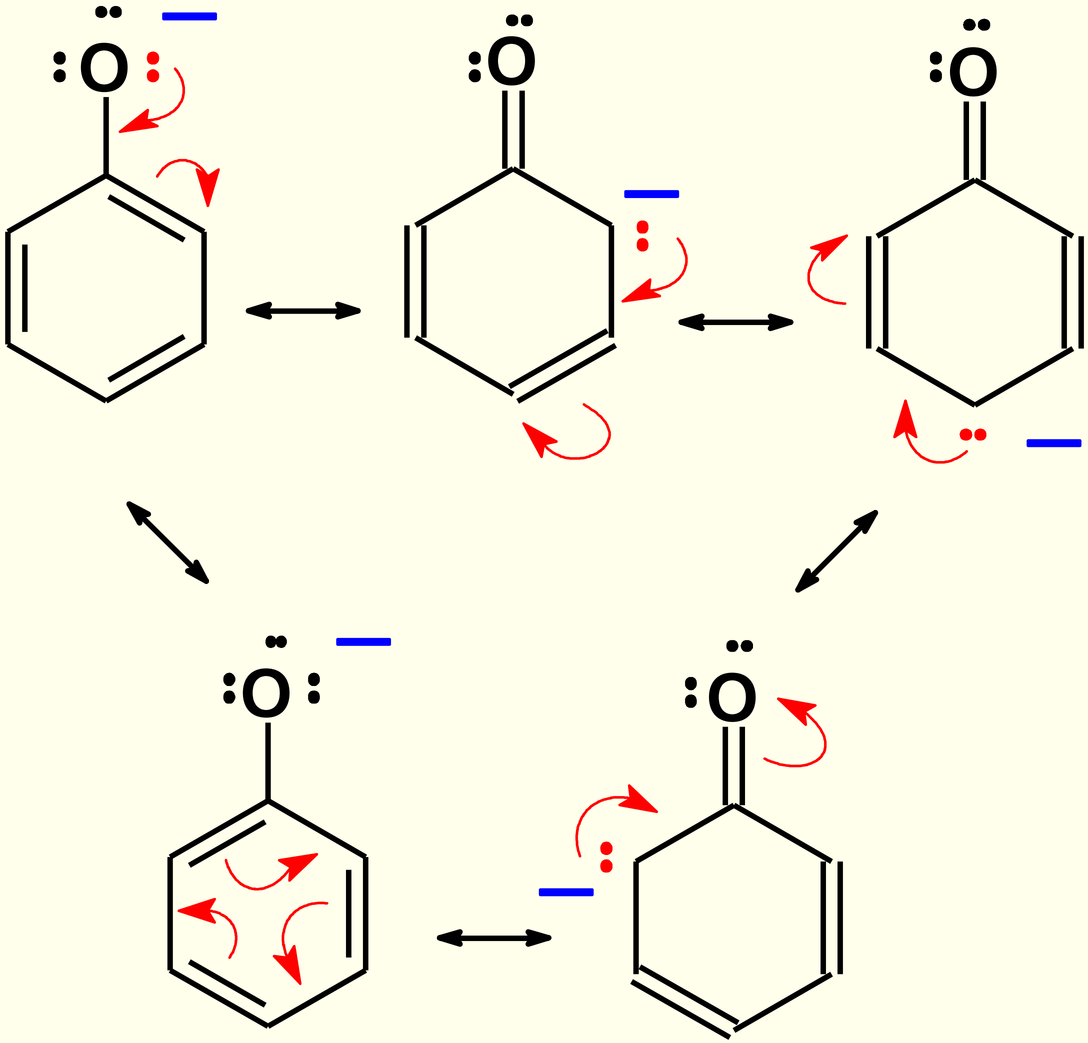
acetic acid

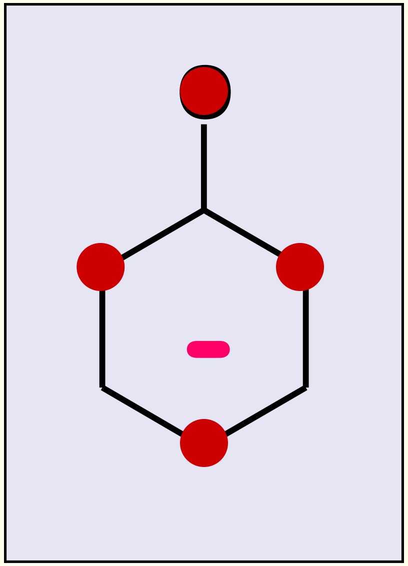


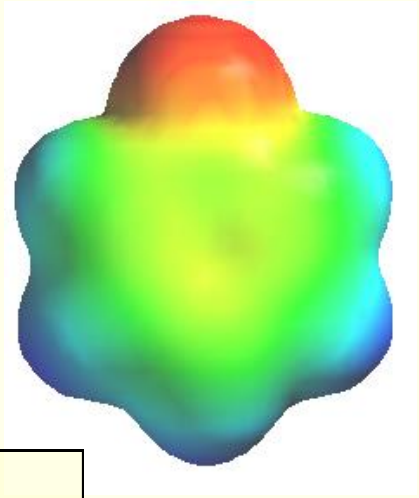
acetate ion



Phenolate ion Resonance







non-equivalent structures
charge on carbon and oxygen

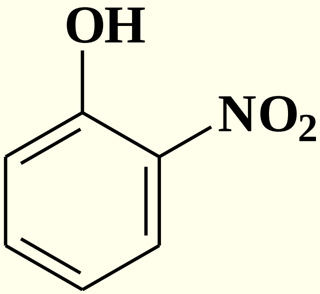
Nitrophenols

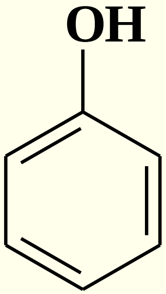
Placing a nitro group on the benzene ring of a phenol increases its acidity.

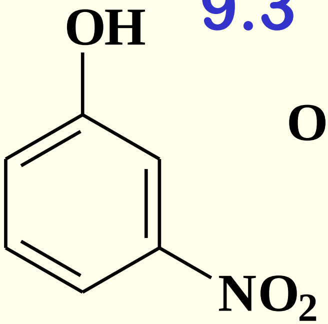
The effect is largest when the nitro group is placed in an *ortho* or a *para* position on the ring, and considerably smaller for the *meta* position.

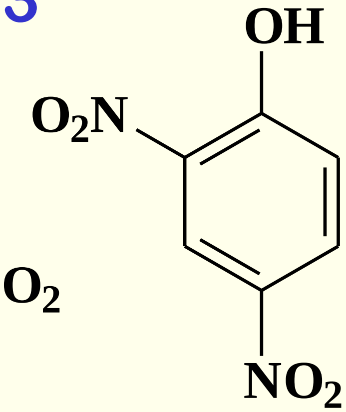
Multiple nitro groups at the ortho and para positions can increase the pKa of a phenol to the point that it becomes a very strong acid.

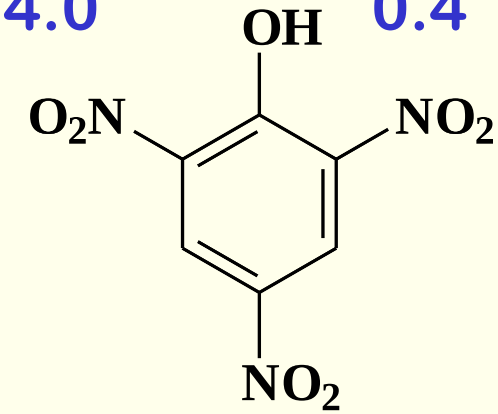
pKa Values of Nitrophenols

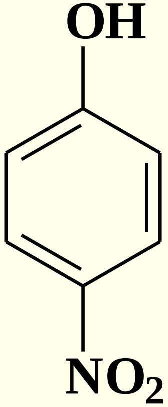

7.2


10

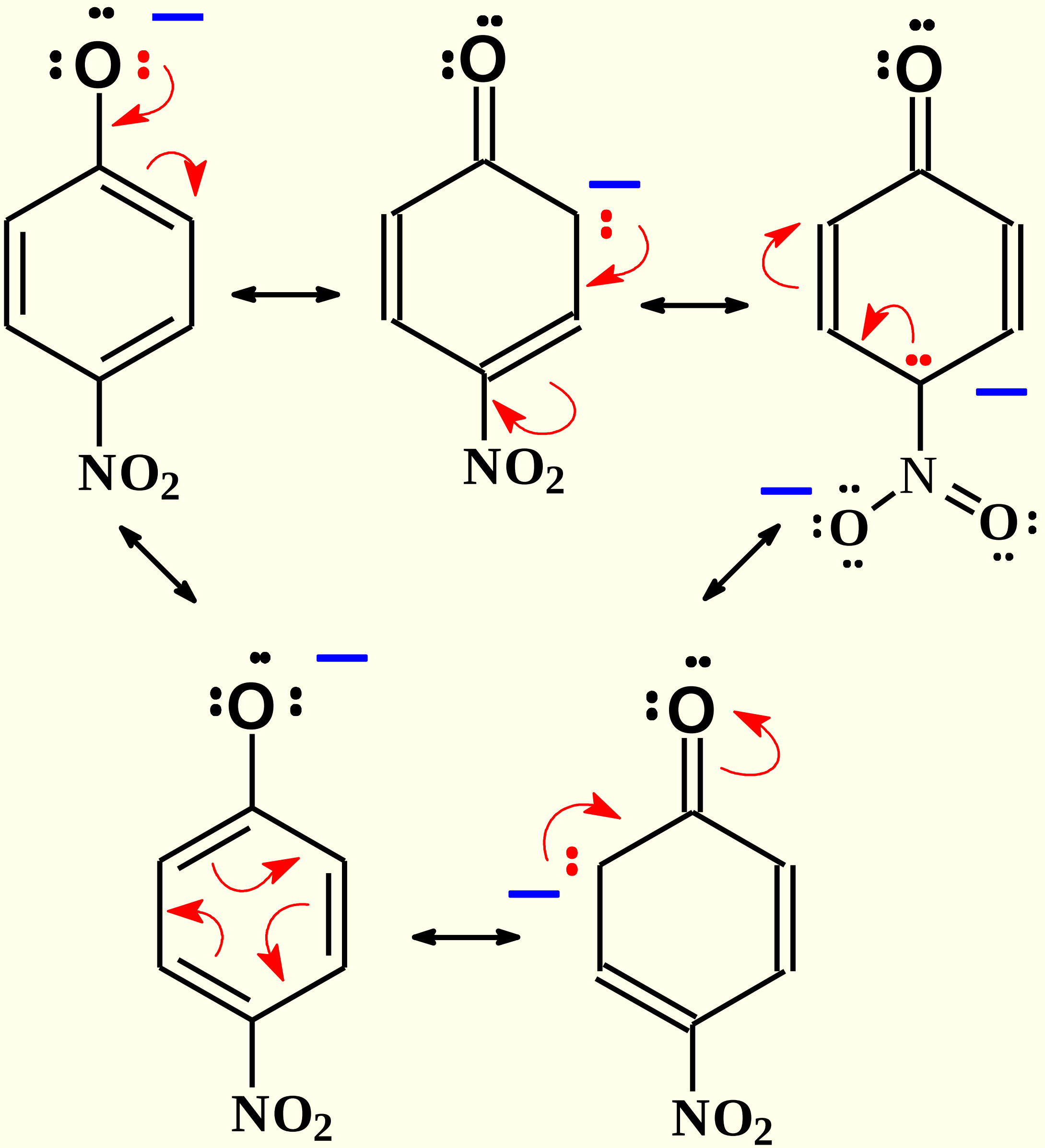

9.3


4.0


0.4

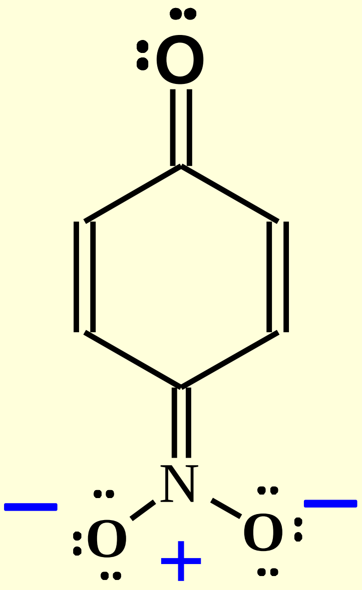

7.3

Resonance in *p*-Nitrophenol

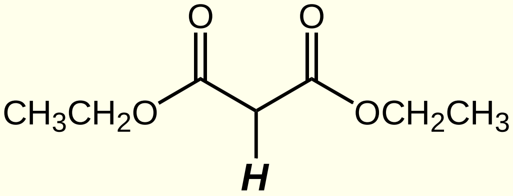
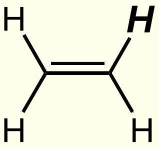
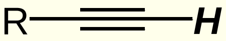
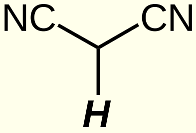
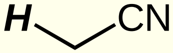
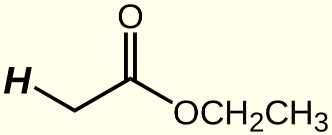
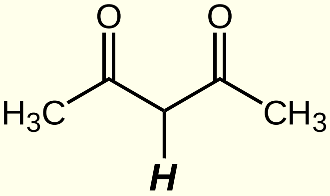
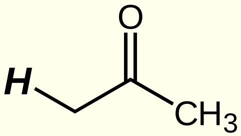
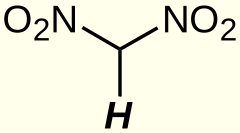


When in an *ortho* or *para* position a nitro group can participate in resonance.

extra structure



Alpha Hydrogen compounds

Acid	pK_a	***Acid***	pK_a
$CH_3CH_2CH_2CH_2\text{-}\boldsymbol{H}$	~50		13
	44		
	25		11
	25	$\boldsymbol{H}\text{-}CH_2NO_2$	10
	24		9
	20		4

Take Away Lession:

Resonance strengthens acid
Resonance weakens base

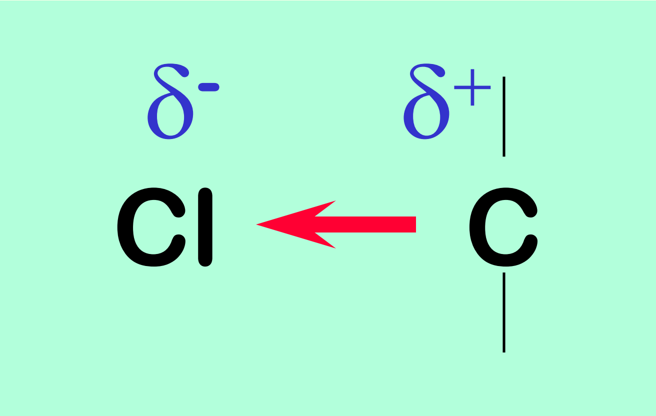
Inductive Effects

Resonance operates through the π bonding system. It doesn't drop off with distance.

Inductive effect operates through the sigma bonding system. It drops off with increasing distance.

Types of Inductive Effects

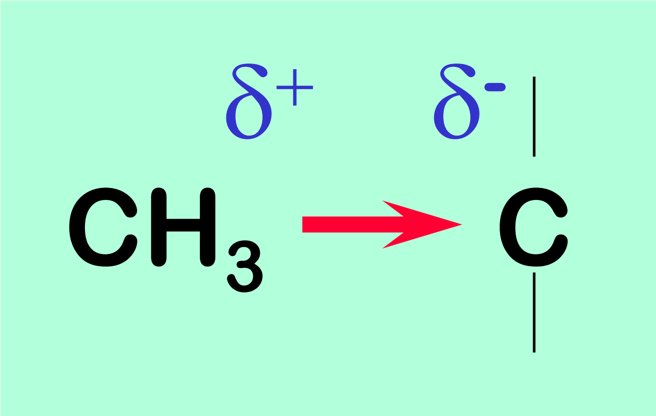
ELECTRON WITHDRAWING GROUPS



F, Cl, Br, NO_2 , NR_3^+

electronegative elements take electron density from cabon. This *strenthens* the acidity.

ELECTRON DONATING GROUPS

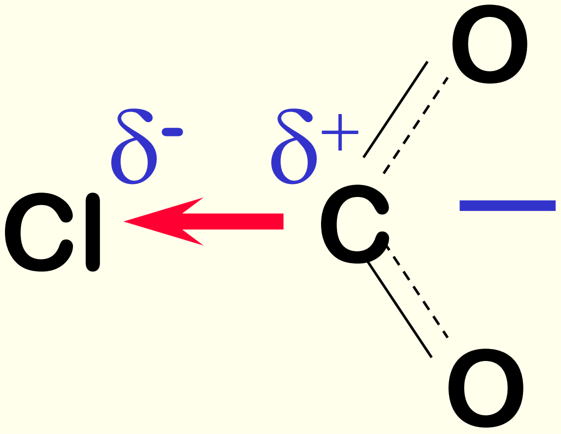


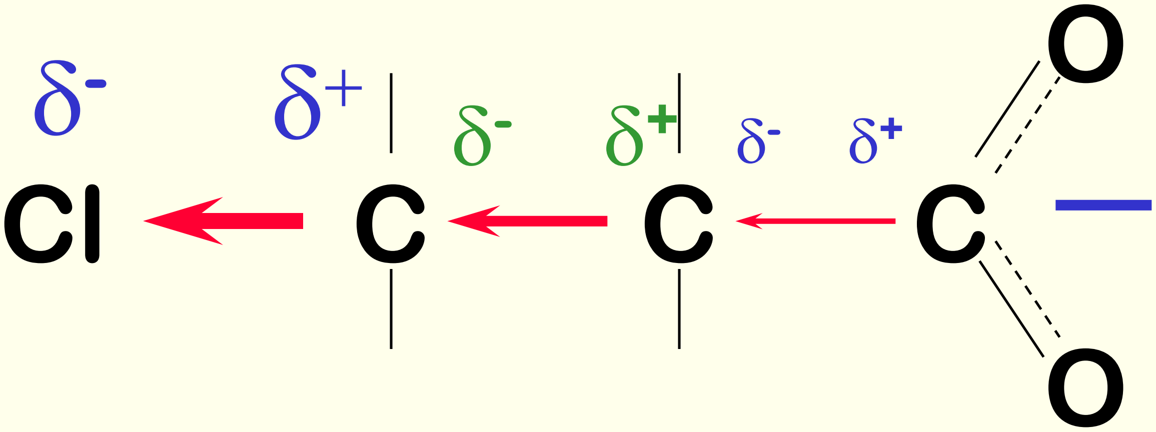
R, CH_3

alkyl groups donate electron density to carbon. This *weakens* the acidity.

Inductive Effects on Haloacids

Chlorine helps to stabilize -CO_2^- by withdrawing electrons





The effect diminishes with distance - it carries for about 3 bonds.

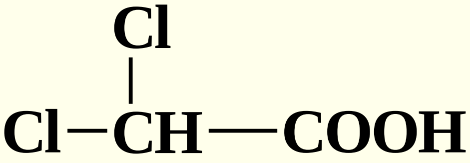
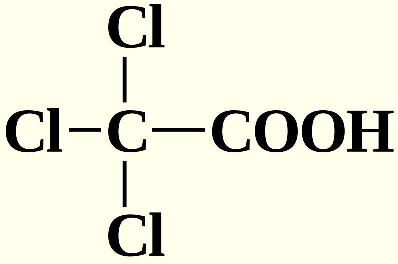
Inductive Effects

pKa Values

increasing electronegativity

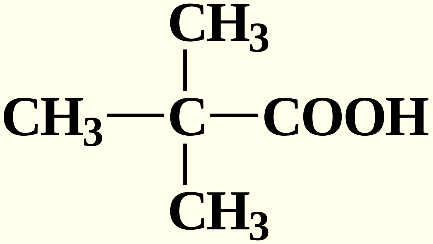
$I-CH_2COOH$	3.13
$Br-CH_2COOH$	2.87
$Cl-CH_2COOH$	2.81
$F-CH_2COOH$	2.66

multiple substituents

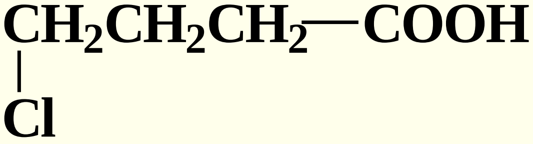
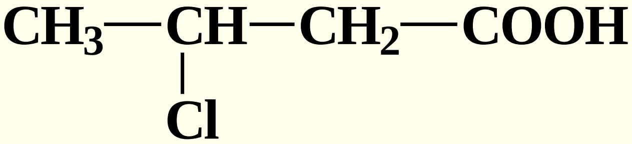
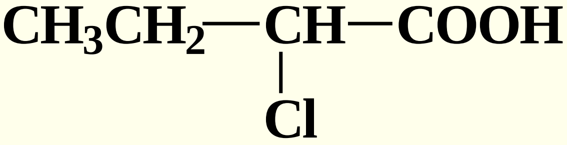
CH_3-COOH	4.75
$Cl-CH_2-COOH$	2.81
 $Cl-CH(Cl)-COOH$	1.29
 $Cl-C(Cl)(Cl)-COOH$	0.65

Inductive Effects

pKa Values

$H-COOH$	3.75
CH_3-COOH	4.75
CH_3CH_2-COOH	4.87
$CH_3CH_2CH_2-COOH$	4.81
 $CH_3-\underset{CH_3}{\overset{CH_3}{\overset{\vert}{\underset{\vert}{C}}}}-COOH$	5.02

Alkyl groups release electrons. This decreases acidity

$CH_3CH_2CH_2-COOH$	4.8
 $\underset{Cl}{\underset{\vert}{CH_2}}CH_2CH_2-COOH$	4.5
 $CH_3-\underset{Cl}{\underset{\vert}{CH}}-CH_2-COOH$	4.0
 $CH_3CH_2-\underset{Cl}{\underset{\vert}{CH}}-COOH$	2.9

↑ distance

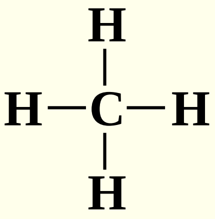
When the chlorine atom is moved further away from the carboxyl group, acidity decreases

Hybridization Effects

Effect of Hybridization

pKa values

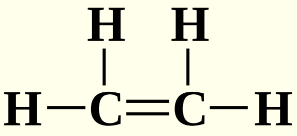
sp^3



CH_4

ca. 50

sp^2



$H_2C=CH_2$

35

sp $H-C\equiv C-H$ 25

sp orbitals are more electron withdrawing than sp^3 orbitals (sp orbitals have more s character).

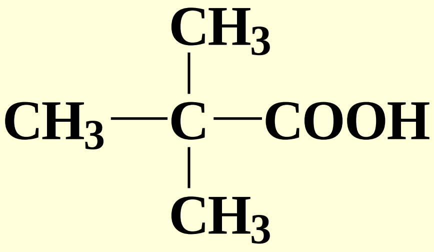
$sp > sp^2 > sp^3$

Solvent Effects

Solvation Effects

CH_3-COOH	4.75
CH_3CH_2-COOH	4.87
$CH_3CH_2CH_2-COOH$	4.81

Notice that these are all similar



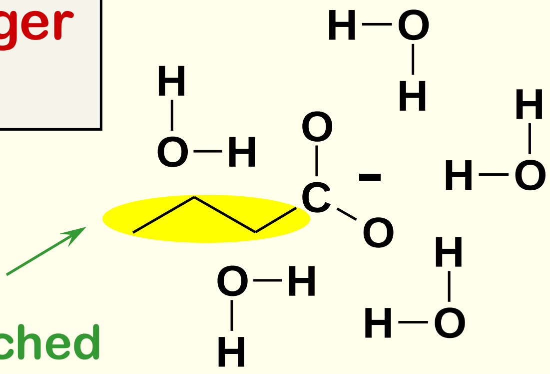
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-COOH$$

5.02

….but this one has a larger pK_a

This is probably a solvation effect.
Solvation lowers the energy of the ion.

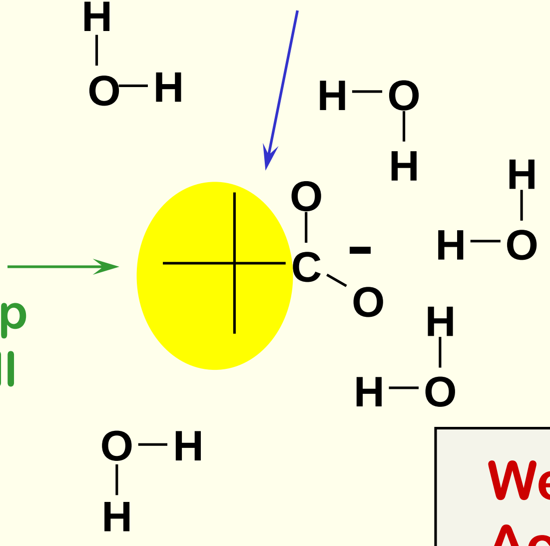
Stronger Acid



unbranched

The bulky *t*-butyl group is not as well solvated.

steric hindrance



Weaker Acid

Intermolecular Attractions

- hydrogen bonding
- dipole-dipole attractions
- London forces or van der Waals attractions

Solubility

SUMMARY

Electronegativity of atom bearing acidic hydrogen; more electronegative = more acidic

Size of atom bearing acidic hydrogen; larger = more acidic.

Resonance: greater charge delocalization in conjugate base = more acidic.

alpha-hydrogens: carbonyls, nitro, cyano, etc. Greater charge delocalization in conjugate base = more acidic.

Inductive effect: electronegative atoms withdraw electrons making the acid more acidic.

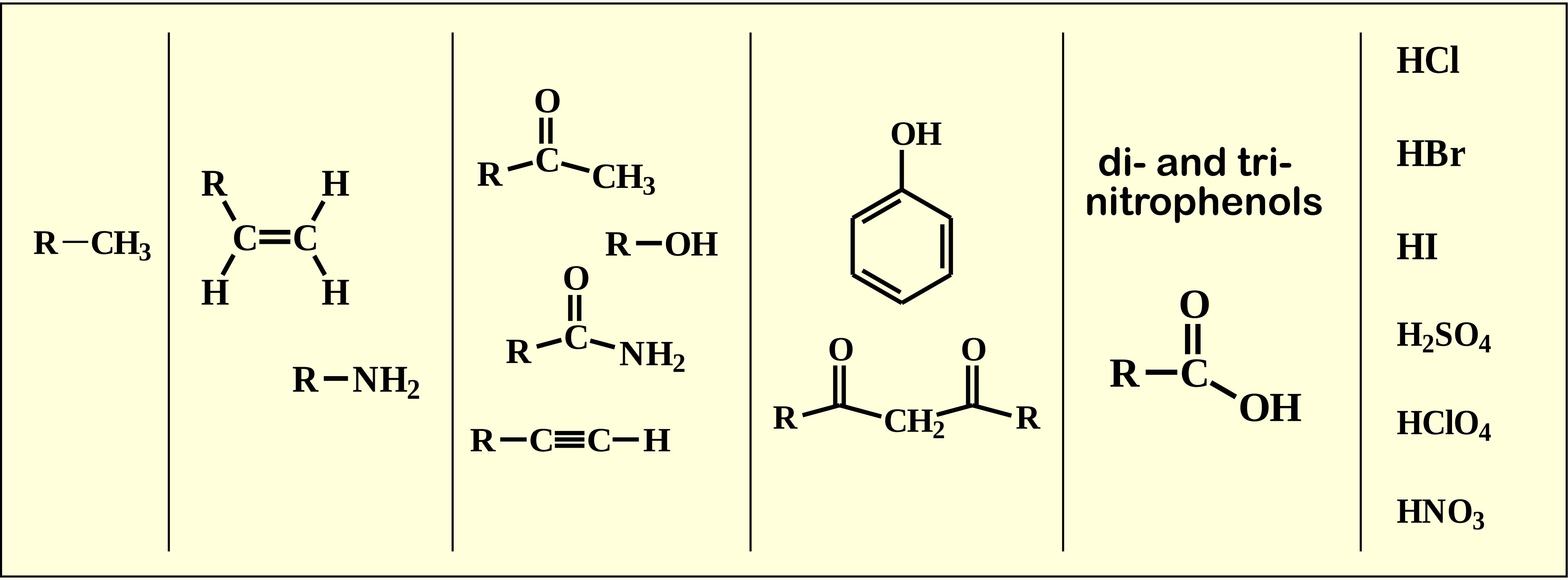
Hybridization; more *s*-character = more acidic

Classification of Weak and Strong Acids by Functional Group

weak acids

strong acids

40 20 10 5 0 pKa



alkanes

alkenes
amines

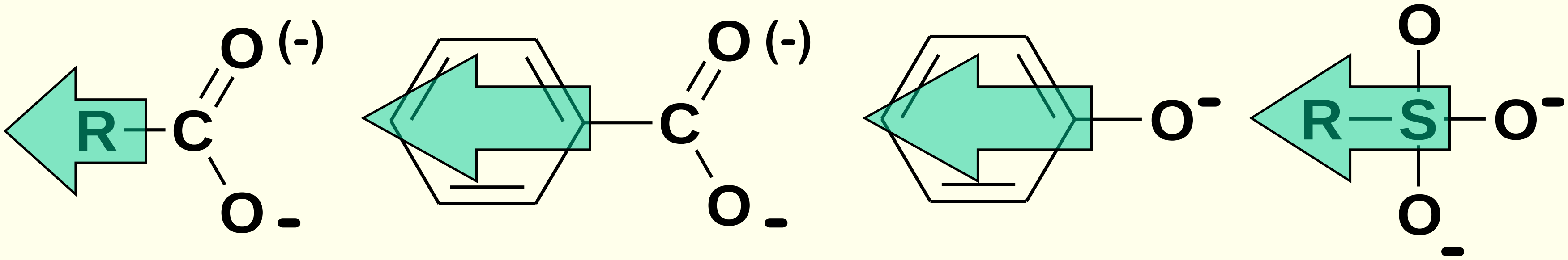
alcohols
ketones
amides
alkynes

phenols
β-diketones

carboxylic acids
nitrophenols

inorganic acids
oxyacids

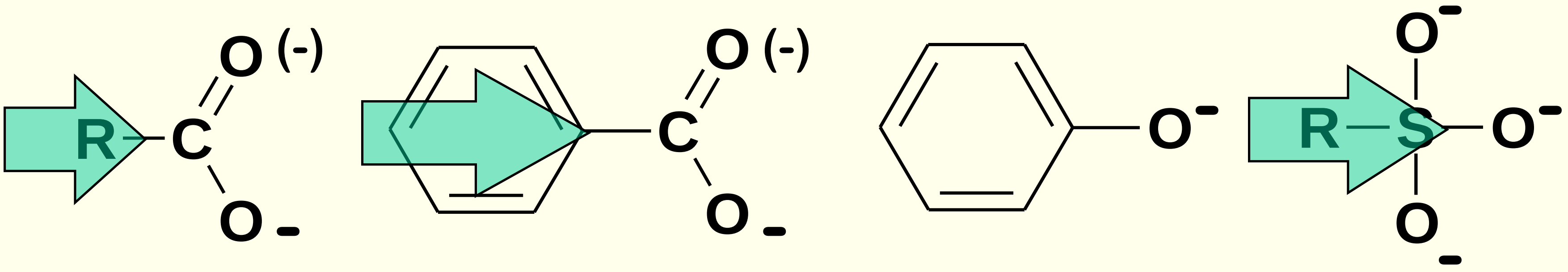
Electron-Withdrawing Effects Strengthen Acids



Any effect that “bleeds” electron density away from the negatively-charged end of the conjugate base will stabilize (lower the energy) of the conjugate base and make it a weaker base.
The parent acid will be a stronger acid.

Conversely .....

Electron-Donating Effects Weaken Acids



Any effect that “pushes” extra electron density toward the negatively-charged end of the conjugate base will destabilize (increase the energy) of the conjugate base and make the base weaker. The parent acid will be stronger.