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.

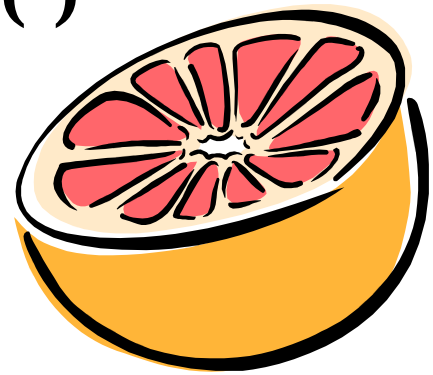
Muitas reações químicas são classificadas como **reações ácido-base**; não são necessariamente neutralizações.

Teoria Ácido-Base

- Como você descreveria um ***ácido*** ou uma ***base***?
  - Questões semelhantes aparecem desde sua decrição no séc. XIII.

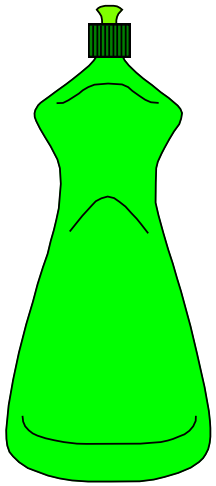
Ácidos

- 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



Acid-Base Theory – Arrhenius (1884)

- Arrhenius defined the terms acid and base as follows:
  - An ***acid*** is a substance that produces H^+ ions when dissolved in water
  - A ***base*** is a substance that produces OH^- ions when dissolved in water

Acid-Base Theory - Arrhenius

$$HNO_3(l) \xrightarrow{H_2O} H^+(aq) + NO_3^-(aq)$$

$$Ca(OH)_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2OH^-(aq)$$

Problems with Arrhenius theory

Like Dalton's atomic theory, Arrhenius theory have problems today:

Acidity did not show in other solvent. What is the solvent role?

Some salts produce acidic or basic solutions, not neutral. Why?

Which is the base, NH_3 or NH_4OH? Is OH^- really the only base?

How can H^+ be stable? Are proton donated?

Some chemists want students to learn Brønsted-Lowry theory of acids and bases before learning Arrhenius theory, because the former is more general.

Brønsted-Lowry Theory

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

Brønsted-Lowry Theory

- In the Bronsted-Lowry definition:

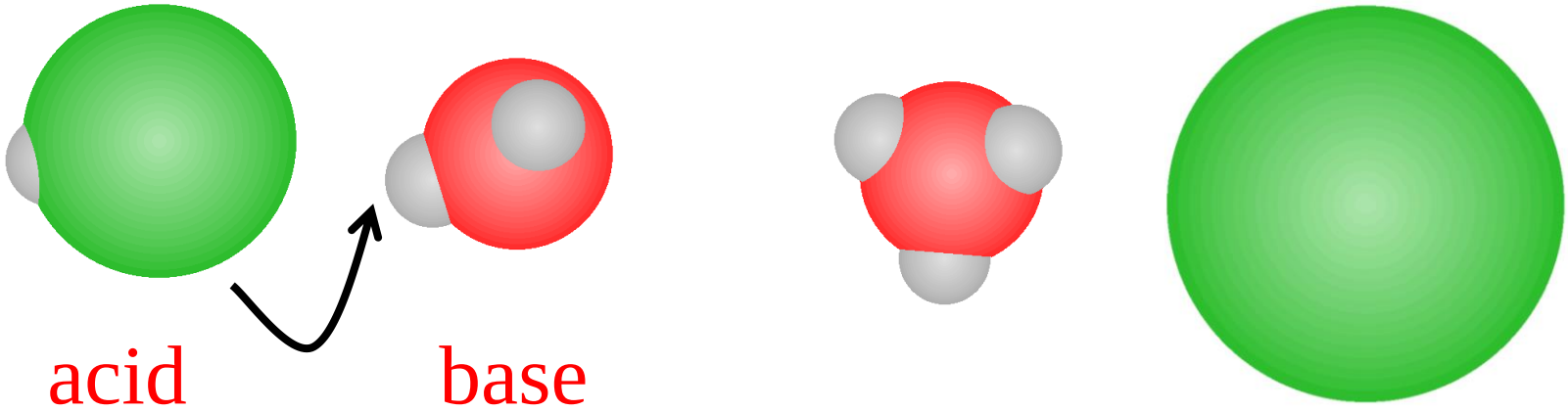
  An ***acid*** is a substance from which a proton can be removed (proton donor)

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

Bronsted-Lowry Concept

Example:

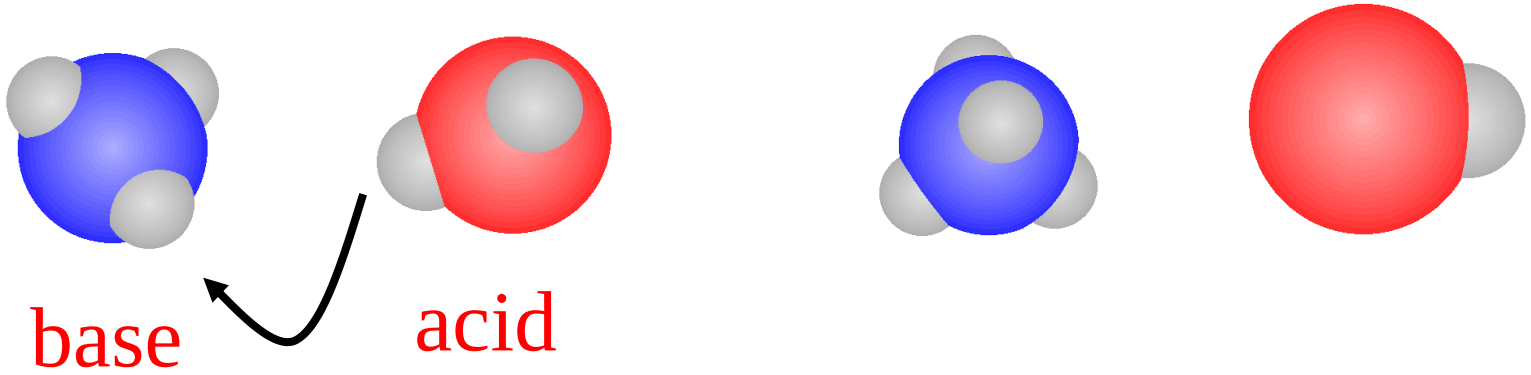
$$HCl + H_2O \Longrightarrow H_3O^+ + Cl^-$$



Bronsted-Lowry Concept

Example:

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



Bronsted-Lowry Concept

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

acid base

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

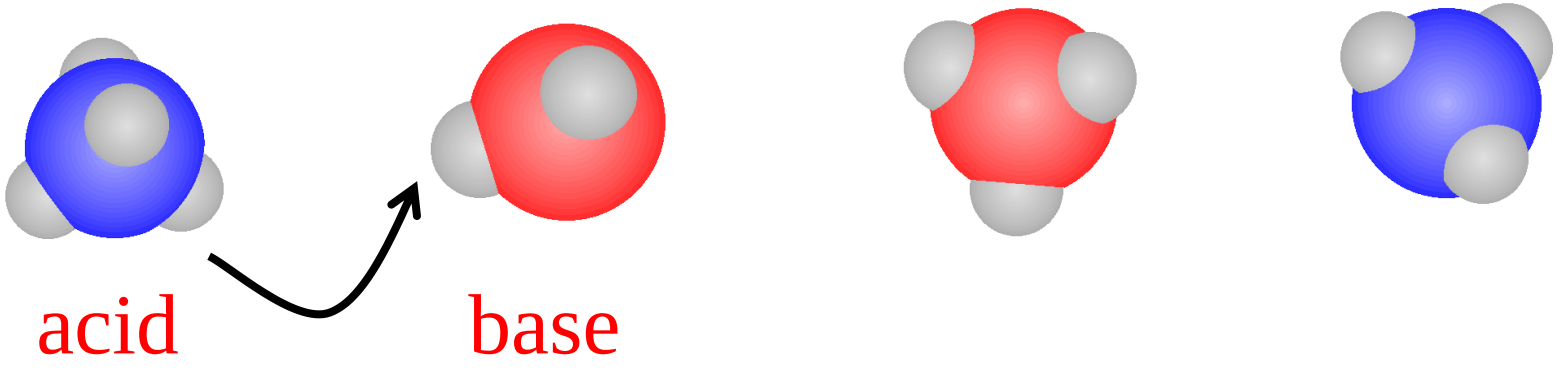
base acid

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

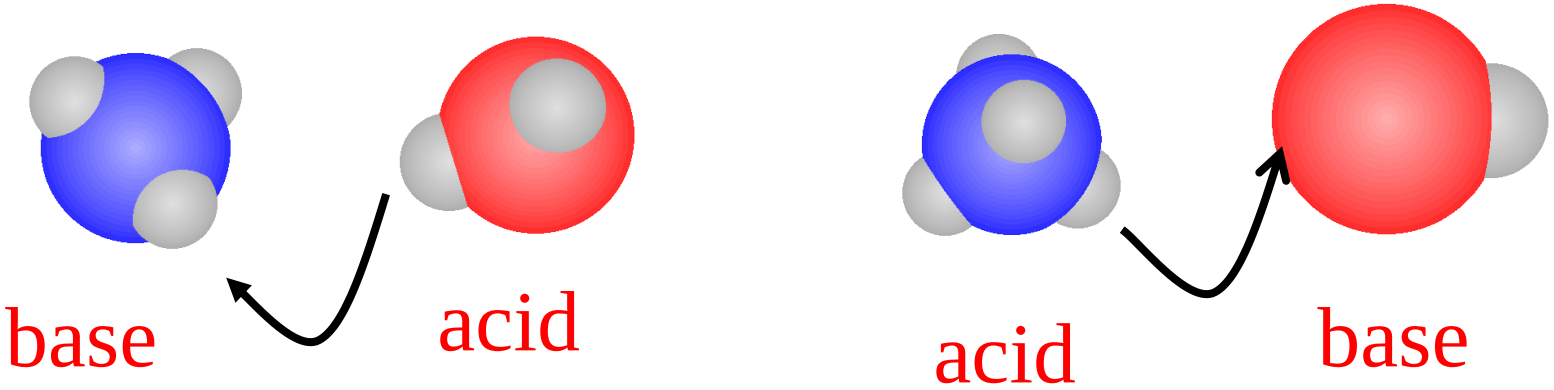
Brønsted-Lowry Concept

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$



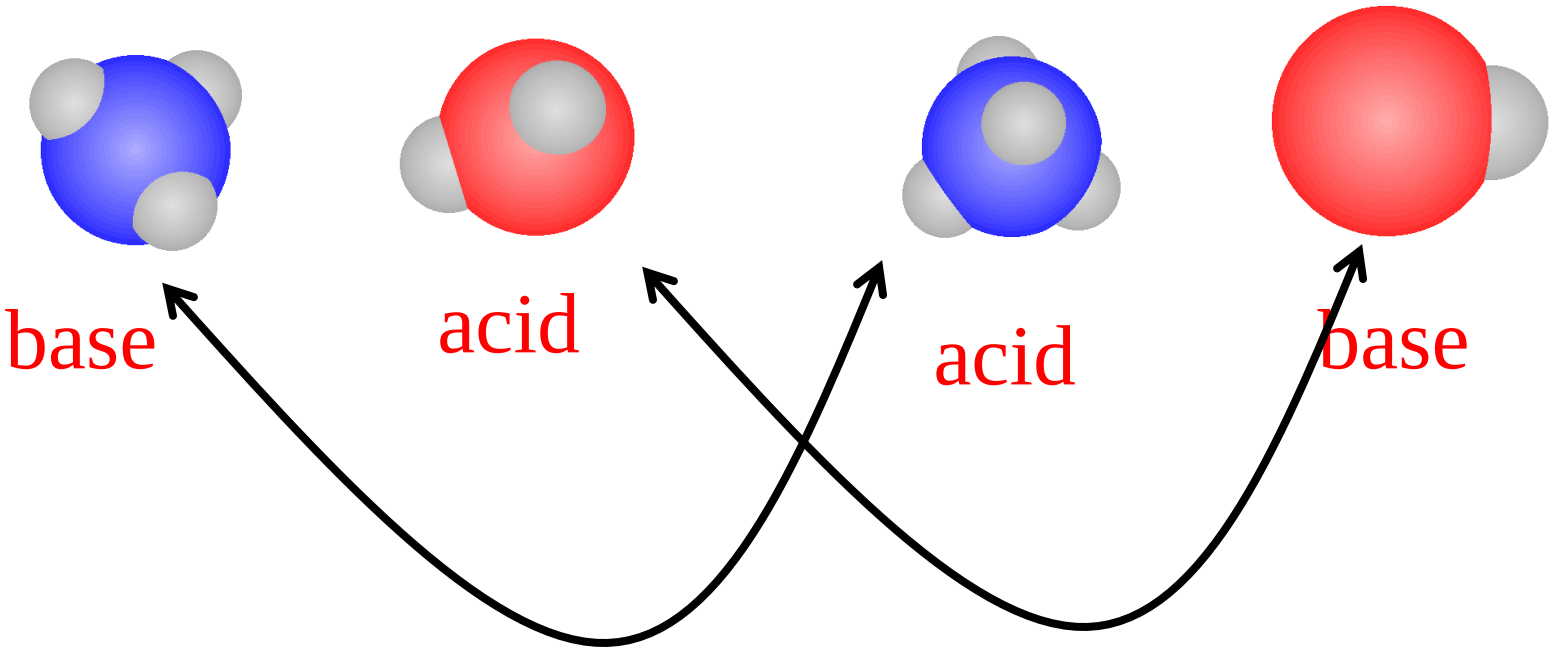
Brønsted-Lowry Concept

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



Brønsted-Lowry Concept

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



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

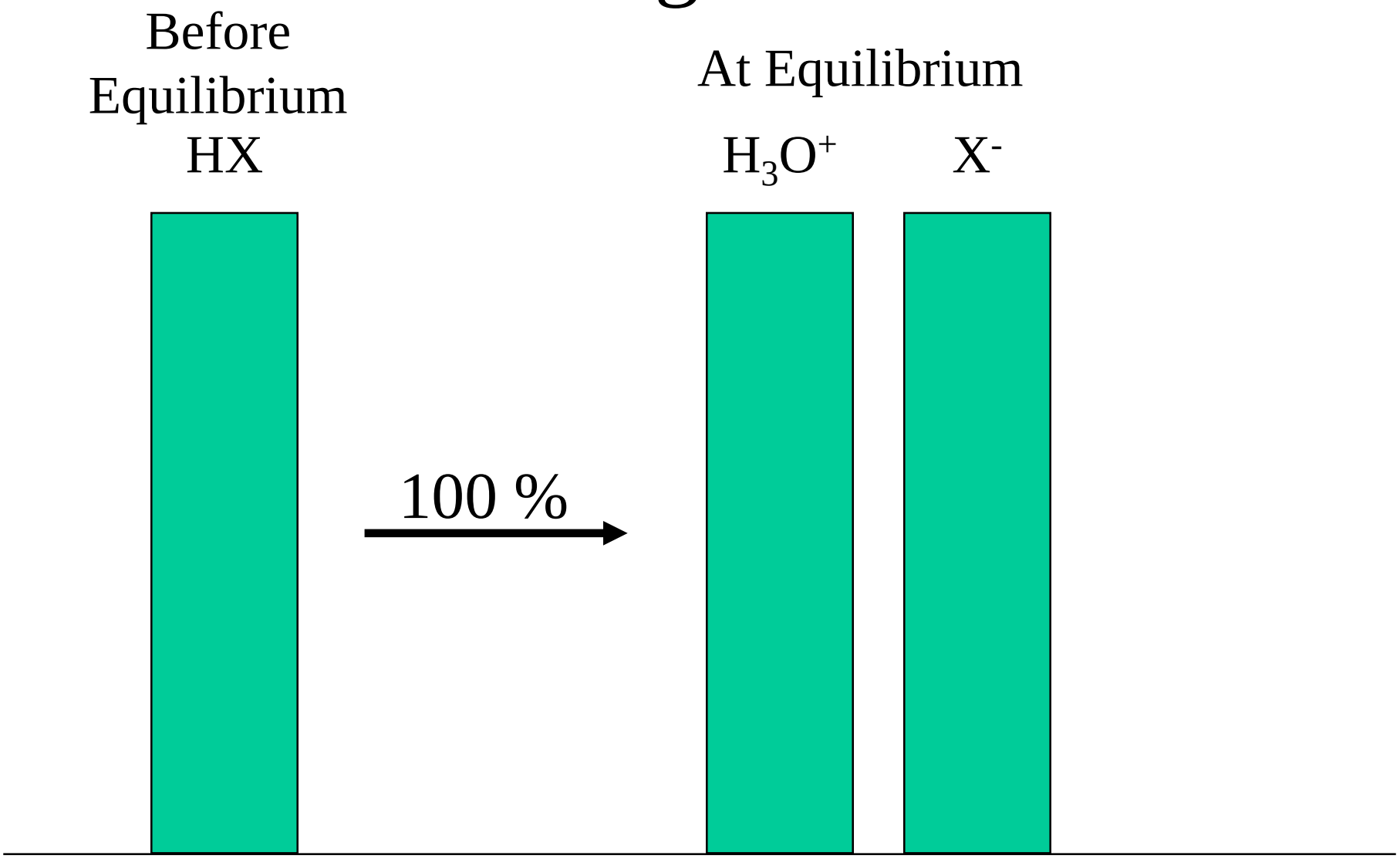
$$HX + H_2O \rightarrow H_3O^+ + X^-$$

- 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



Acid-Base Strength

- Common Strong Acids (Know these!)

  HCl

  HBr

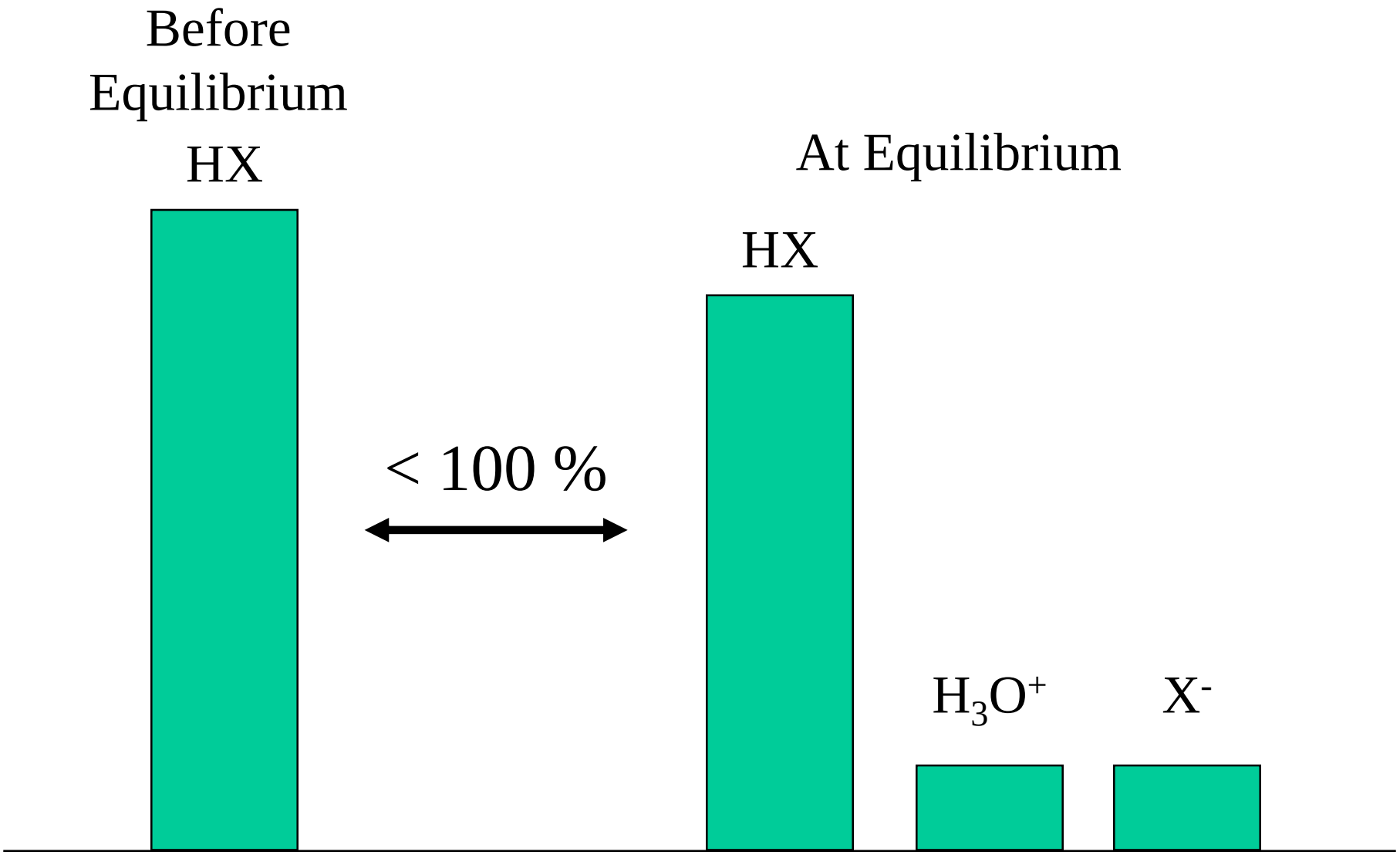
  HI

  HNO_3

  $HClO_4$

  H_2SO_4

Weak Acids



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

Strongest base that can exist in H_2O

More on Neutralization Reactions

- Acids react with bases:
  - acid + base $\rightarrow$ salt + water

  or
  - acid + base $\rightarrow$ salt

Autoionization of Water

- In pure water, the following equilibrium occurs: $H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$
- The equilibrium constant for this reaction is the ion product, K_w:

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

– $[H_3O^+] = [OH^-] = 1 \times 10^{-7}$ M (25 °C)

so

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

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).

pH = – log [H⁺]; $[H^+] = 10^{-pH}$

pOH = – log [OH⁻]; $[OH^-] = 10^{-pOH}$

p*K* = – log [*K*]; $K = 10^{-pK}$

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;

$K_w = [H^+]\,[OH^-]$

$-\log K_w = pH + pOH = 14$ only at 25°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.

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^-

$pK_a = 9.1$ $pK_b = 4.9$

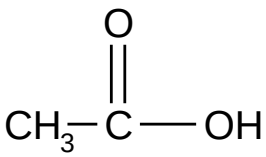
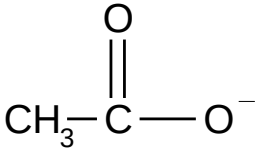
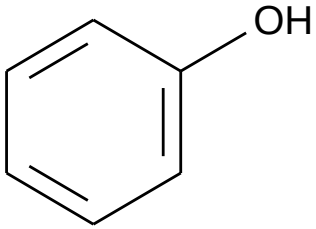
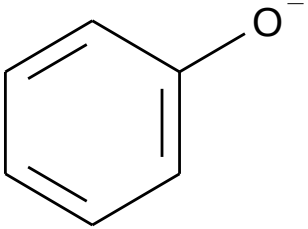
pK_a

$$pK_a = -\log K_a$$

Strong acid = large K_a = small pK_a

Weak acid = small K_a = large pK_a

Relative Acid and Base Strengths

ACID	CONJ. BASE	K_a	pK_a
$HClO_4$	ClO_4^-	10^{10}	-10
		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

stronger

ACID STRENGTH

weaker

weaker

BASE STRENGTH

stronger

Acid Strengths

Strong Acid

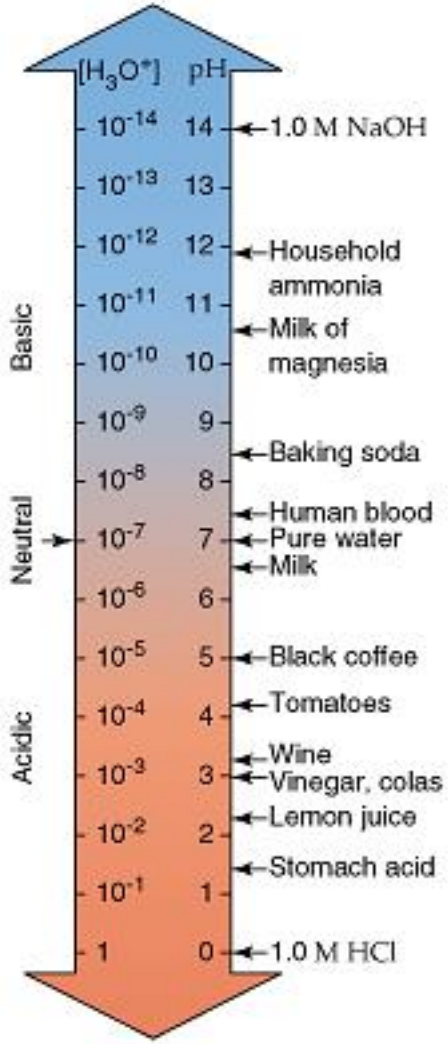
Conjugate base is weak

pK_a is small

Weak Acid

Conjugate base is strong

pK_a is large


[H3O+]
pH
10-14
14
1.0 M NaOH
10-13
13
10-12
12
Household ammonia
10-11
11
Milk of magnesia
10-10
10
Basic
10-9
9
Baking soda
10-8
8
Human blood
Neutral
10-7
7
Pure water
Milk
10-6
6
10-5
5
Black coffee
10-4
4
Tomatoes
Acidic
Wine
10-3
3
Vinegar, colas
10-2
2
Lemon juice
Stomach acid
10-1
1
1
0
1.0 M HCl

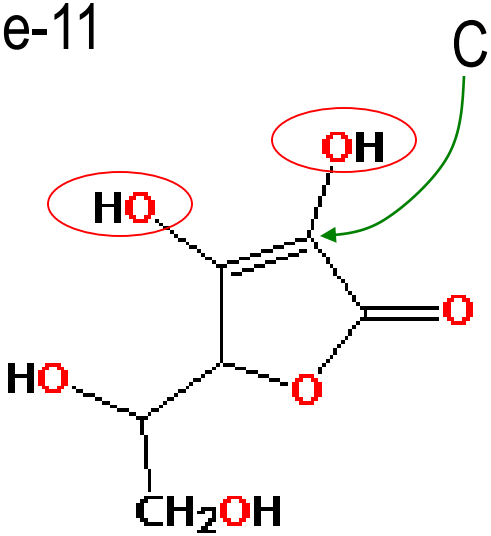
Polyprotic acids

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

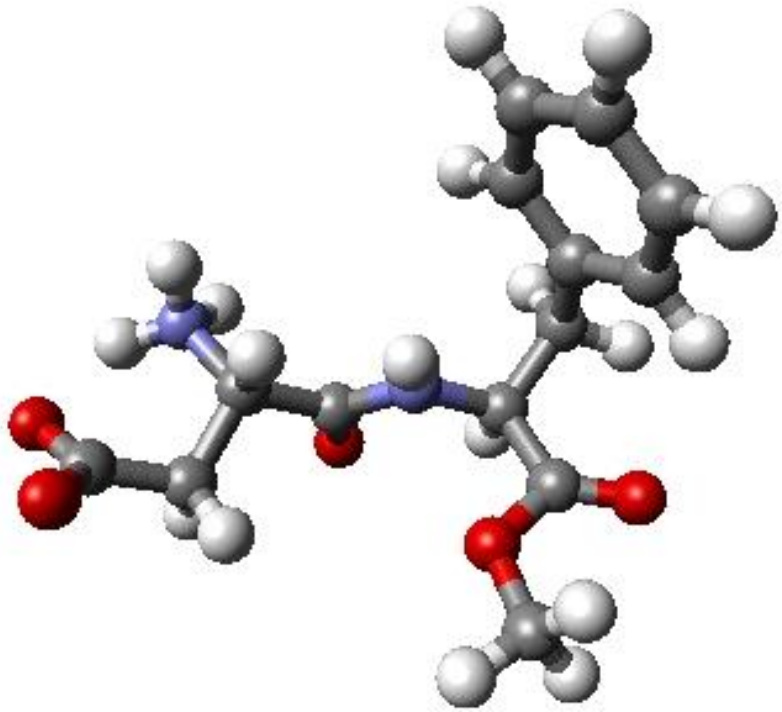
$H_2SO_4 = H^+ + HSO_4^-$ K_{a1} very large completely ionized
$HSO_4^- = H^+ + SO_4^{2-}$ $K_{a2} = 0.012$

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

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



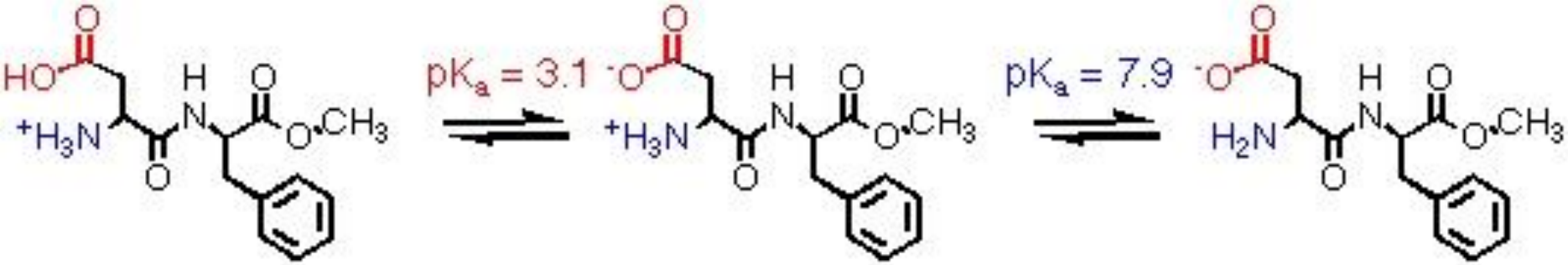
Others:
H_2S, H_2SO_3, H_3PO_4, $H_2C_2O_4$ (oxalic acid) …



Aspartame - nutrasweet

A dipeptide methyl ester :
L-aspartyl-L-phenylalanine methyl ester
$C_{14}H_{18}N_2O_5$ (molar mass = 294.31)

Aspartame has two ionizable protons



Isoelectric point = 5.2

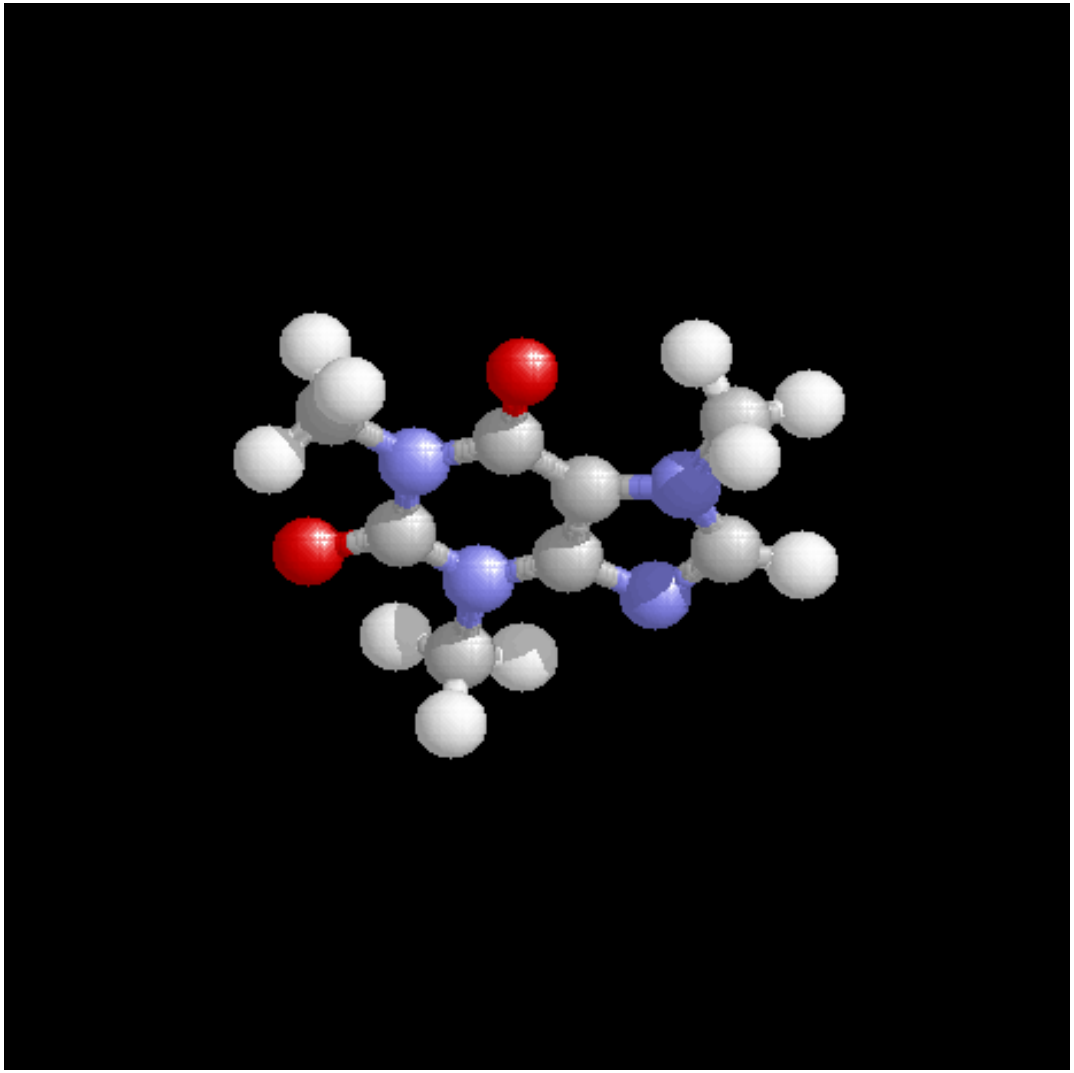
1965. Jim Schlatter synthesized it and discovered it sweet leaving no bitter after tast.

Caffeine

Caffeine $C_8H_{10}N_4O_2$ is a weak base, (**pH of 1% soln 6.9**) taste bitter smell like tea, a cardiac stimulant, (boost of energy), mild diuretic, addictive, operates using the same mechanisms that amphetamines, cocaine and heroin use to stimulate the brain.

Crystals are hexagonal prisms by sublimation, mp 238°C. Sublimes 178°. Fast sublimation is obtained at 160-165° under 1 mm Hg pressure.

Many organic bases are interesting drugs, and their chemistry is fascinating.



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

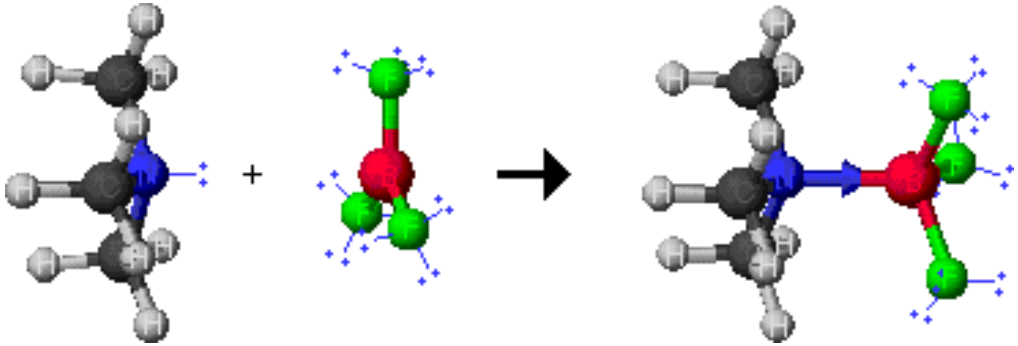
Proposed another method of defining acids and bases. **Lewis acid** - Any substance that can accept a pair of nonbonding electrons.

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

B: → **A**

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

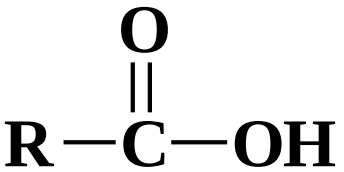
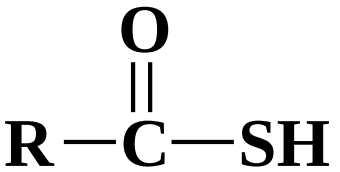
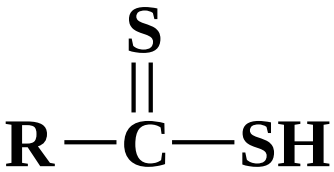
C	N	O	F
Si	P	S	Cl
		Se	Br
			I

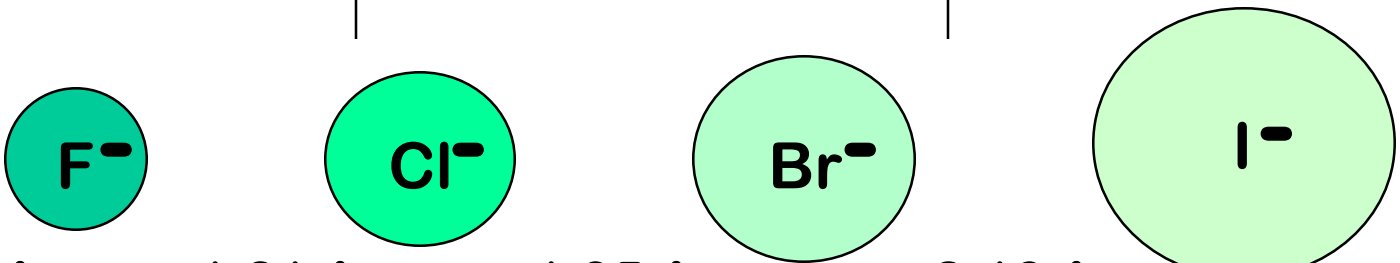
increased size increases acidity

Effect of Atomic Size on Acidity

increasing atom size

pKa Values

HF	3.5	HOH	16		5
HCl	-7	HSH	7		
HBr	-9	HSeH	4		
HI	-10	HTeH	3		



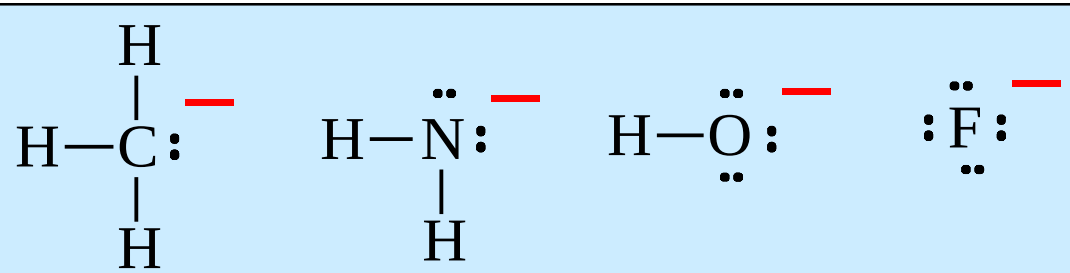
1.36 A 1.81 A 1.95 A 2.16 A

Effect of Electronegativity on Acidity

increasing electronegativity

pKa Values

CH_4	>45	RCH_3	45	$R-C(=O)-CH_3$	20
NH_3	34	RNH_2	35	$R-C(=O)-NH_2$	15
H_2O	16	ROH	18	$R-C(=O)-OH$	5
HF	3.5				



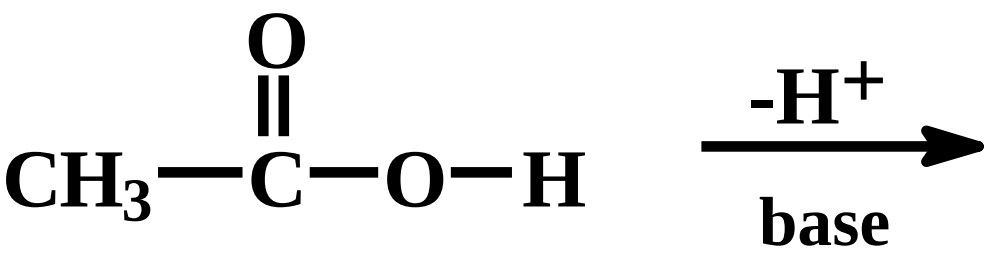
Resonance Effects

Take Away Lession:

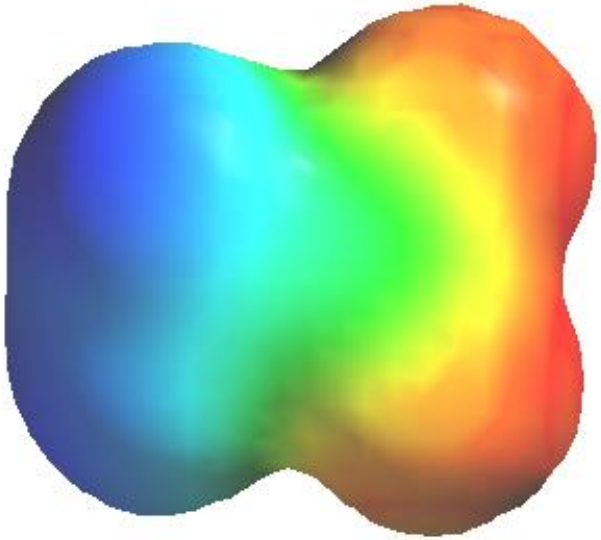
Resonance strengthens acid
Resonance weakens base

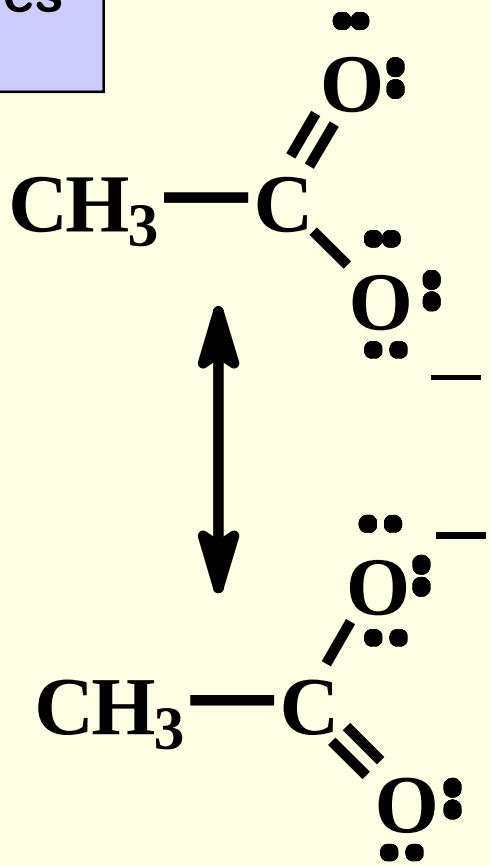
Resonance in the Acetate Ion

equivalent structures
charge on oxygens



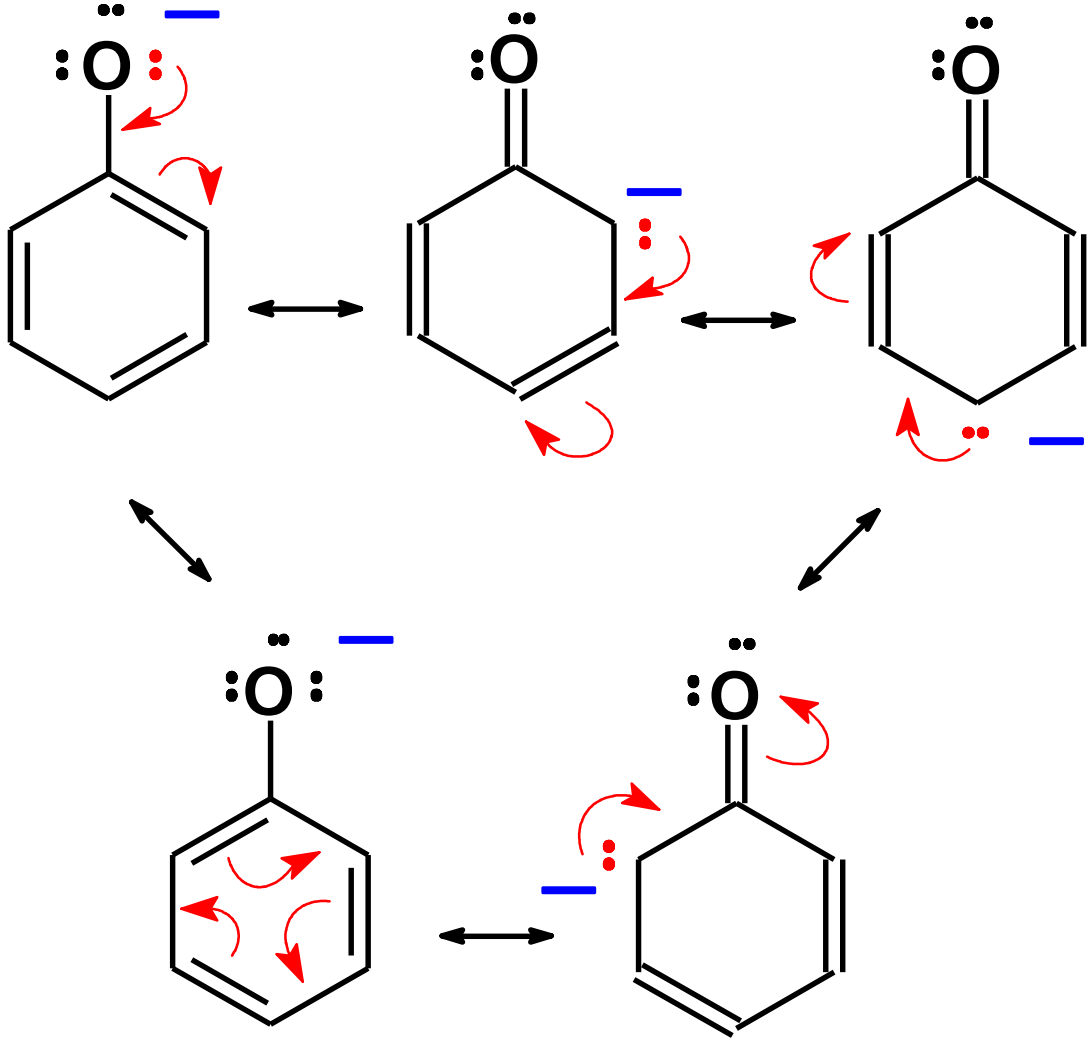
acetic acid

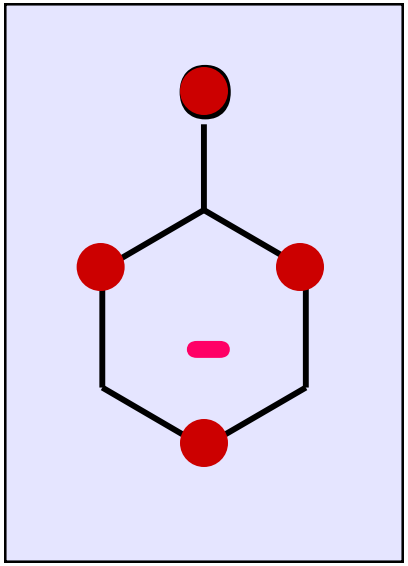


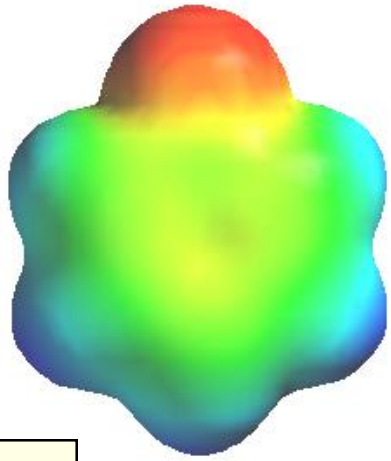


acetate ion

Phenolate ion Resonance







non-equivalent structures
charge on carbon and oxygen

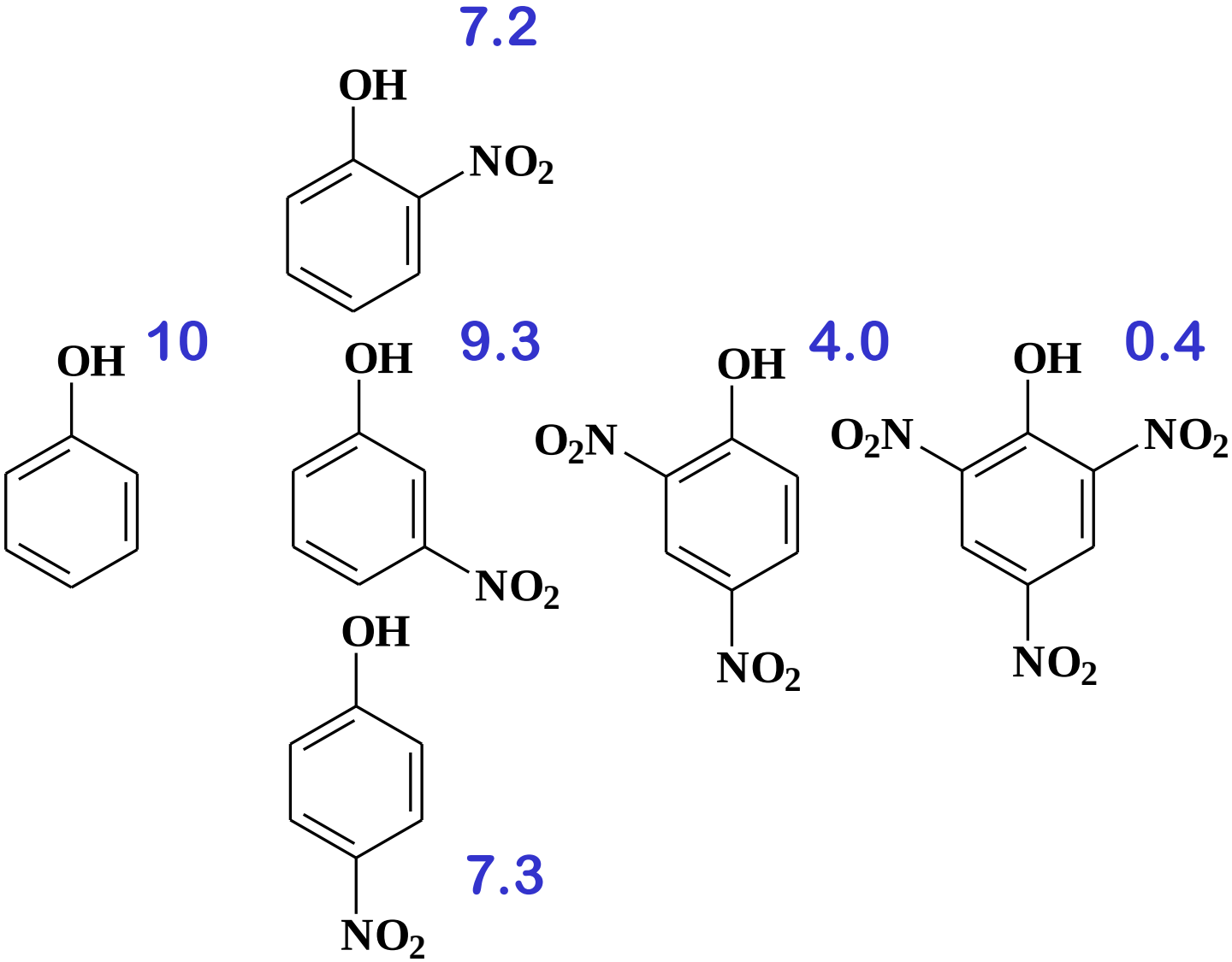
Nitrophenols

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

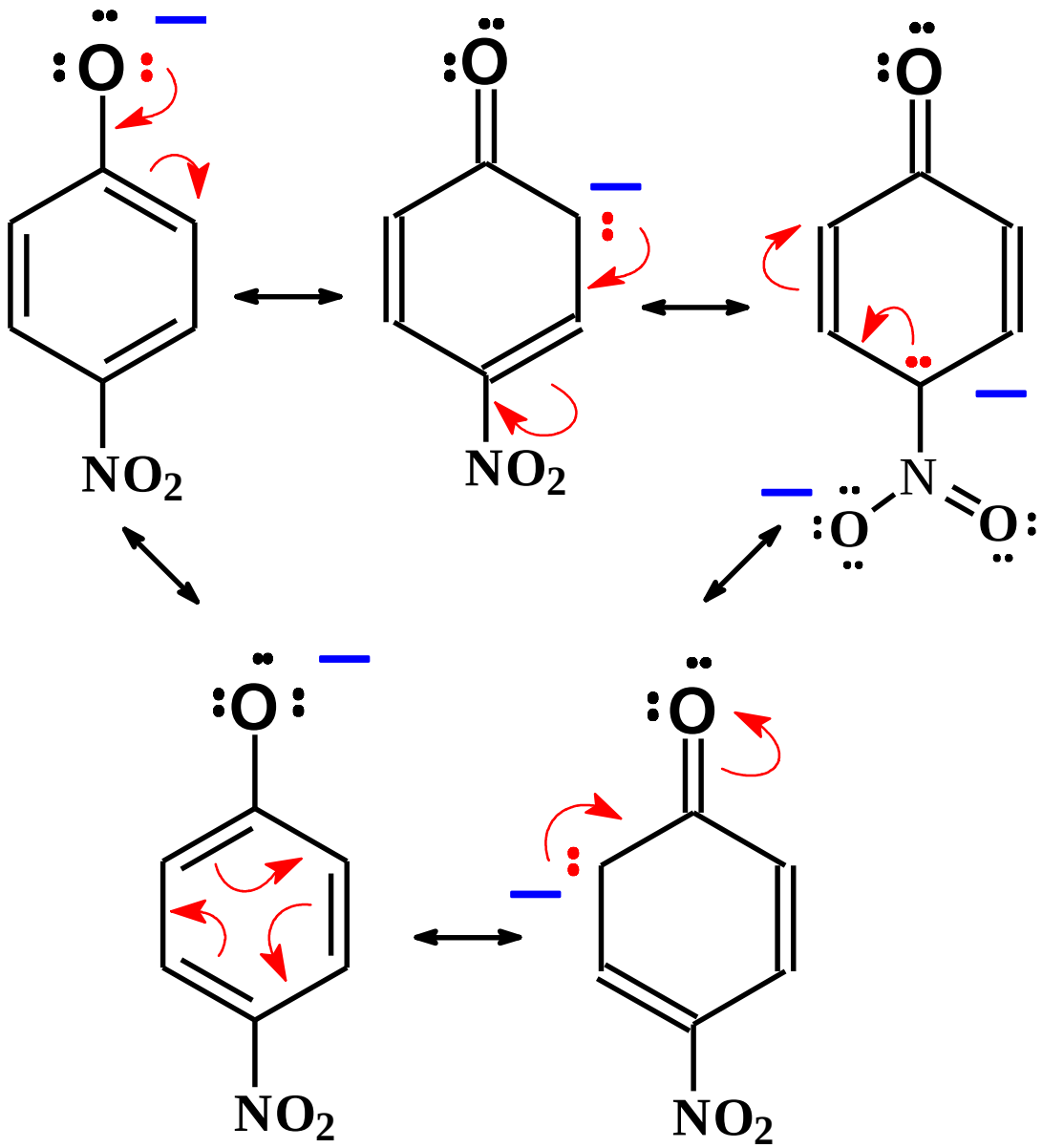
The effect is largest when the nitro group is placed in an *ortho* or a *para* position on the ring, and considerably smaller for the *meta* position.

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

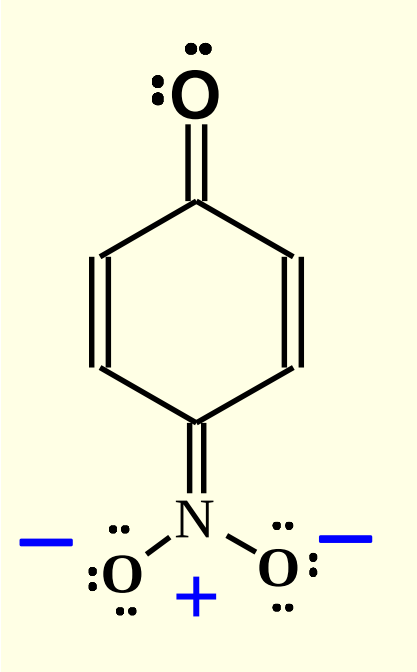


Resonance in *p*-Nitrophenol

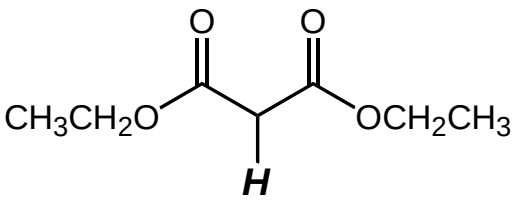
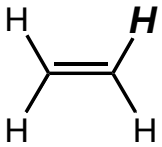
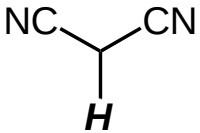
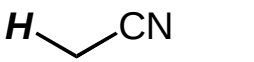
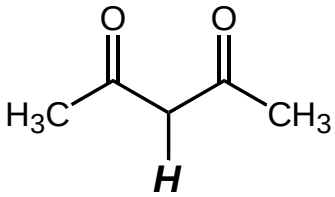
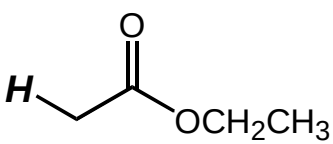
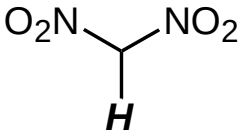
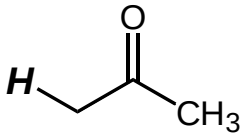


When in an *ortho* or *para* position a nitro group can participate in resonance.

extra structure



Alpha Hydrogen compounds

Acid	***pK***$_a$	***Acid***	***pK***$_a$
$CH_3CH_2CH_2CH_2$-***H***	~50		13
	44		11
	25	***H***-CH_2NO_2	10
	25		9
	24		4
	20		

Take Away Lession:

Resonance strengthens acid
Resonance weakens base

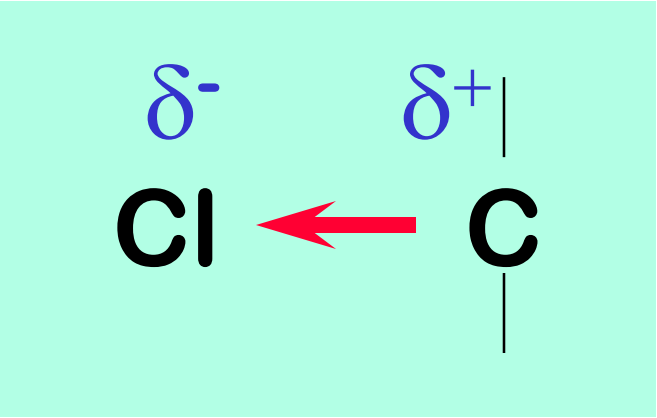
Inductive Effects

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

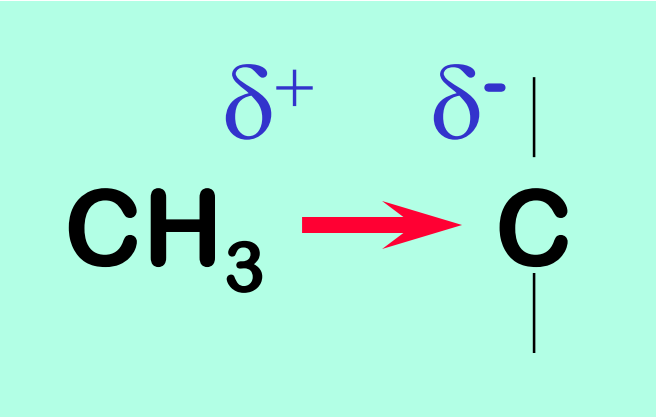
ELECTRON WITHDRAWING GROUPS



F, Cl, Br, NO_2 , NR_3^+

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

ELECTRON DONATING GROUPS

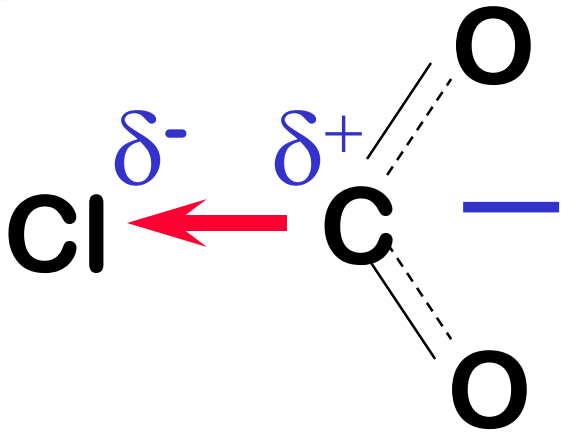


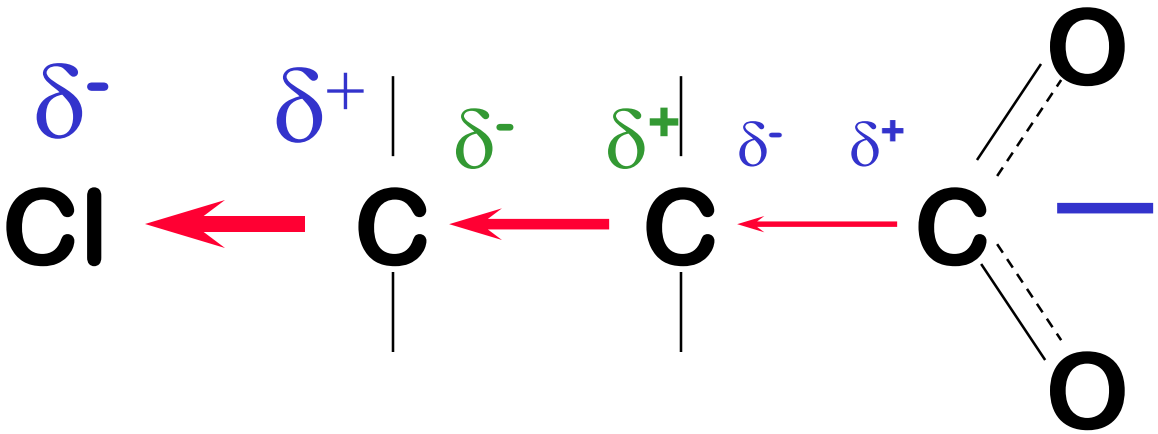
R, CH_3

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

increasing electronegativity

multiple substituents

pKa Values

$I—CH_2COOH$	3.13	CH_3-COOH	4.75
$Br—CH_2COOH$	2.87	$Cl-CH_2-COOH$	2.81
$Cl—CH_2COOH$	2.81	$Cl-CH(Cl)—COOH$	1.29
$F—CH_2COOH$	2.66	$Cl-C(Cl)_2—COOH$	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
$CH_3—C(CH_3)_2—COOH$	5.02

Alkyl groups release electrons. This decreases acidity

$CH_3CH_2CH_2—COOH$	4.8
$CH_2(Cl)CH_2CH_2—COOH$	4.5
$CH_3—CH(Cl)—CH_2—COOH$	4.0
$CH_3CH_2—CH(Cl)—COOH$	2.9

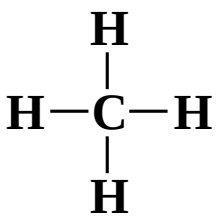
distance

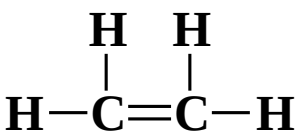
When the chlorine atom is moved further away from the carboxyl group, acidity decreases

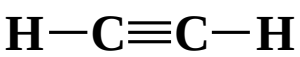
Hybridization Effects

Effect of Hybridization

pKa values

sp^3  ca. 50

sp^2  35

sp  25

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

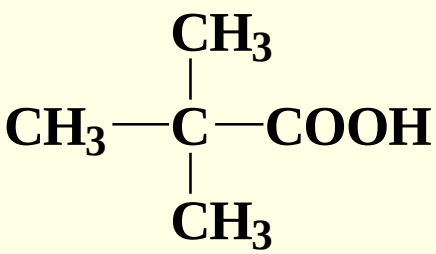
$sp > sp^2 > sp^3$

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

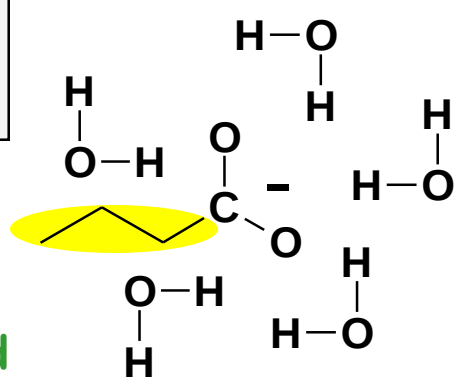


5.02

....but this one has a larger pK_a

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

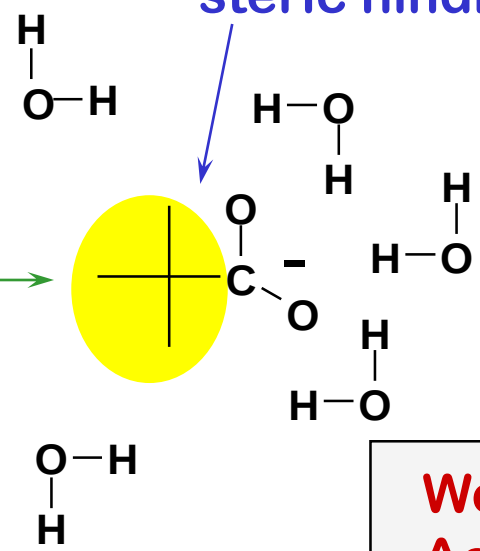
Stronger Acid



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.**

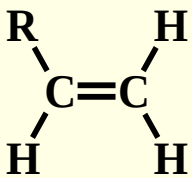
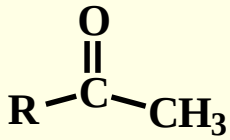
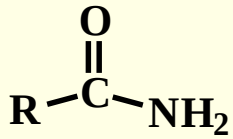
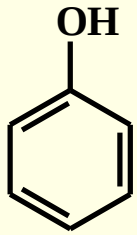
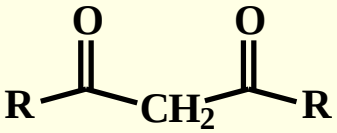
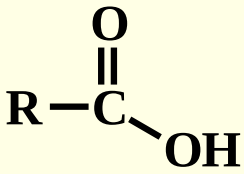
Inductive effect: electronegative atoms withdraw electrons making the acid more acidic.

Hybridization; **more *s*-character = more acidic**

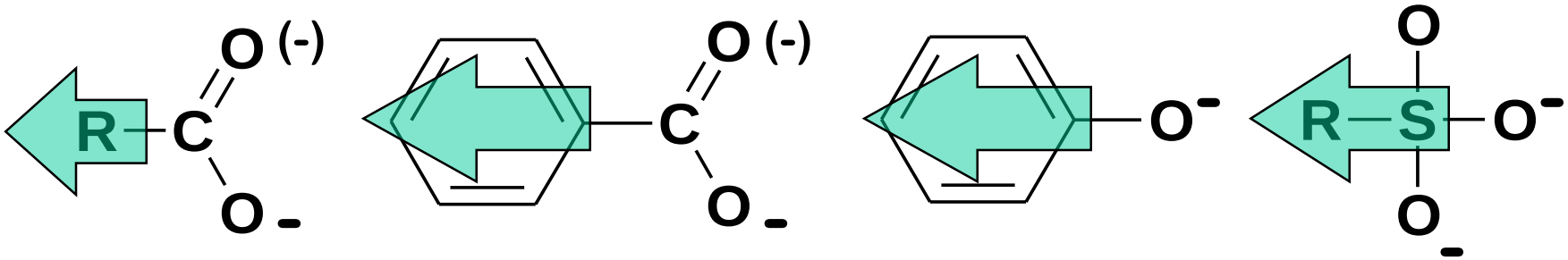
Classification of Weak and Strong Acids by Functional Group

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
$R-CH_3$	 $R-NH_2$	 $R-OH$  $R-C\equiv C-H$	 	di- and tri-nitrophenols 	HCl HBr HI H_2SO_4 $HClO_4$ HNO_3

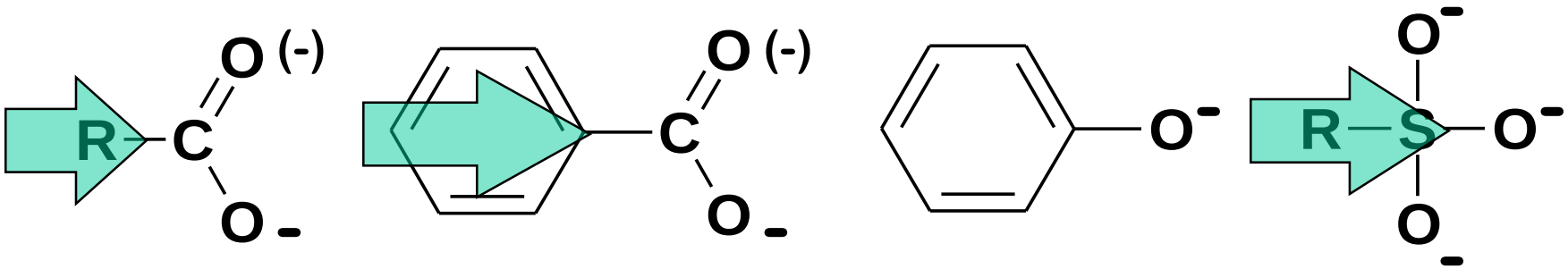
Electron-Withdrawing Effects Strengthen Acids



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.