A Short Introduction on

Acid and Bases

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General Properties

ACIDS

- Taste sour
- Turn **blue** litmus **red**
- React with active metals – Fe, Zn
- React with bases

BASES

- Taste bitter
- Turn **red** litmus **blue**
- Feel soapy or slippery
- React with acids

Three Definitions of Acid

Svante August Arrhenius
Swedish chemist (1859-1927);
Nobel Prize in Chemistry, 1903
•Arrhenius equation
(activation energy)

Who	Theory: Acid=	When
Arrhenius	produce H^+ (only in Water)	1880's
Brønsted	proton(H+) donor (any solvent)	1923
Lowry	-do-	1923
Lewis	Electron-pair acceptor	1923

Arrhenius Acids and Bases

- **Acid**: Substance that, when dissolved in water, increases the concentration of hydrogen ions (protons, H^+).

$$HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$$

- **Base**: Substance that, when dissolved in water, increases the concentration of hydroxide ions.

$$NaOH(aq) \rightleftharpoons Na^+(aq) + OH^-(aq)$$

Is NH_3 a base?

Brønsted–Lowry Acid and Bases

- Brønsted–Lowry: must have *both*

Is BF_3 an acid?

1. an Acid: **Proton donor**

$$HCl(aq) + H_2O \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

2. a Base: **Proton acceptor**

$$HCl + H_2O \rightleftharpoons [Cl^- \cdots H^+ \cdots H_2O] \rightleftharpoons H_3O^+ + Cl^-$$

$$NH_3 + H_2O \rightleftharpoons [NH_3 \cdots H^+ \cdots OH^-] \rightleftharpoons NH_4^+ + OH^-$$

Brønsted-Lowry acids and bases are always paired:
The Brønsted-Lowry acid donates a proton, while the Brønsted-Lowry base accepts it.

A Brønsted–Lowry acid…

…must have a removable (acidic) proton.

HCl, H_2O, H_2SO_4

A Brønsted–Lowry base…

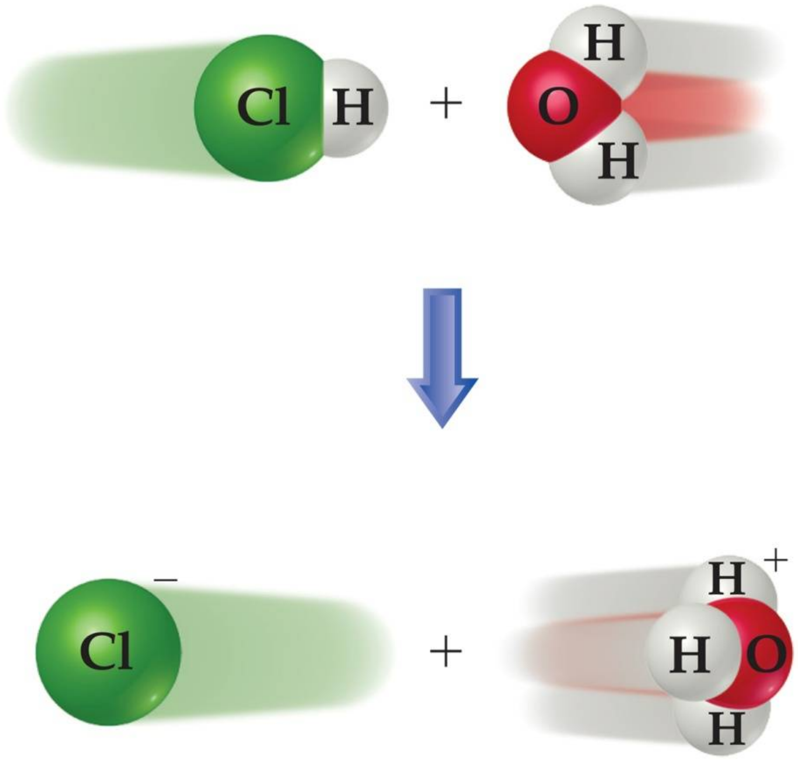
…must have a pair of nonbonding electrons.

NH_3, H_2O

If it can be either…called amphiprotic

e.g. HCO_3^-, HSO_4^-, H_2O etc.

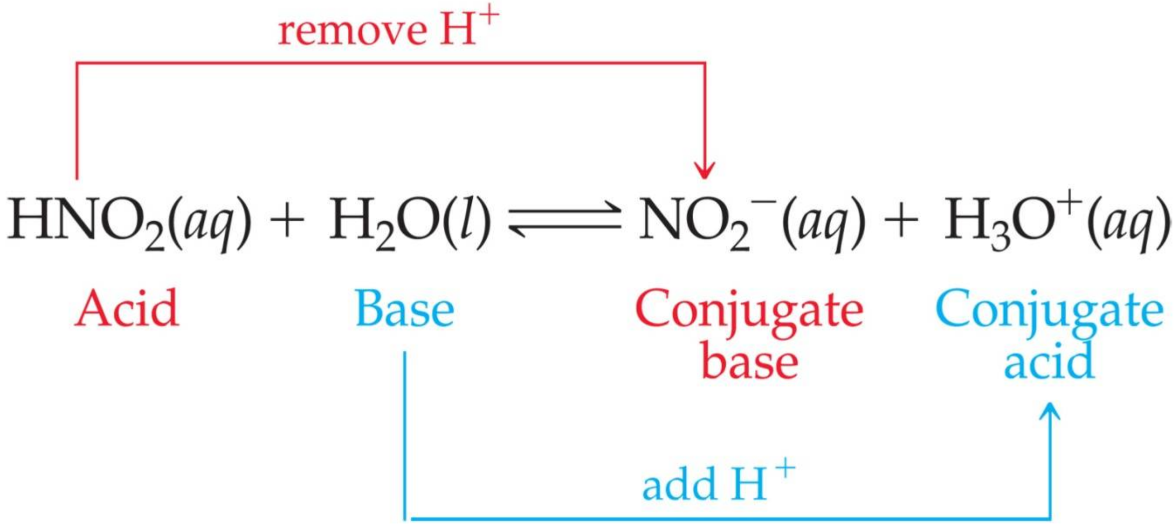
What Happens When an Acid Dissolves in Water?



- Water acts as a Brønsted–Lowry base and abstracts a proton (H^+) from the acid.
- As a result, the conjugate base of the acid and a hydronium ion are formed.

Conjugate Acids and Bases

- From the Latin word *conjugare*, meaning “to join together.”
- Reactions between acids and bases always yield their conjugate bases and acids.



$$HNO_2 + H_2O \rightleftharpoons [NO_2^- \cdots H^+ \cdots H_2O] \rightleftharpoons NO_2^- + H_30^+$$

Lux-Flood Concept

Acids are oxide acceptors, and

Bases are oxide donors.

acid - oxide ion (O^{2-}) acceptor

base - oxide ion (O^{2-}) donor

ex. · $CaO + SiO_2 \rightarrow CaSiO_3$ (= $Ca^{2+}[SiO_3]^{2-}$)

base   acid

Lux-Flood Reactions

Acids are oxide acceptors, bases are oxide donors

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

base acid

$$CaO + H_2O \longrightarrow Ca^{2+} + 2\ OH^-$$

basic anhydride

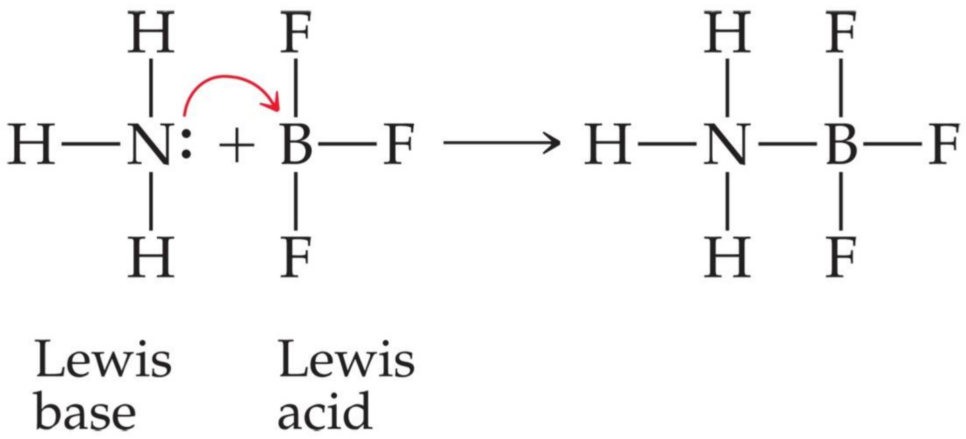
$$SiO_2 + H_2O \longrightarrow H_2SiO_3$$

acidic anhydride

Base: $ZnO + S_2O_7^{2-} = Zn^{2+} + 2SO_4^{2-}$

Acid: $Na_2O + ZnO = Na_2ZnO_3$

Lewis Acids and Bases



- Lewis acids are defined as **electron-pair acceptors**.
- Atoms with an empty valence orbital can be Lewis acids.
- A compound with **no H's** can be a Lewis acid.

- Lewis bases are defined as **electron-pair donors**.
- **Brønsted–Lowry base is also a Lewis base**.

Usanovich Concept

An acid is any chemical species which

i) reacts with a base, or

ii) accepts anions or electrons, or

iii) furnish cations;

and

A base is any chemical species that would

i) react with an acid, or

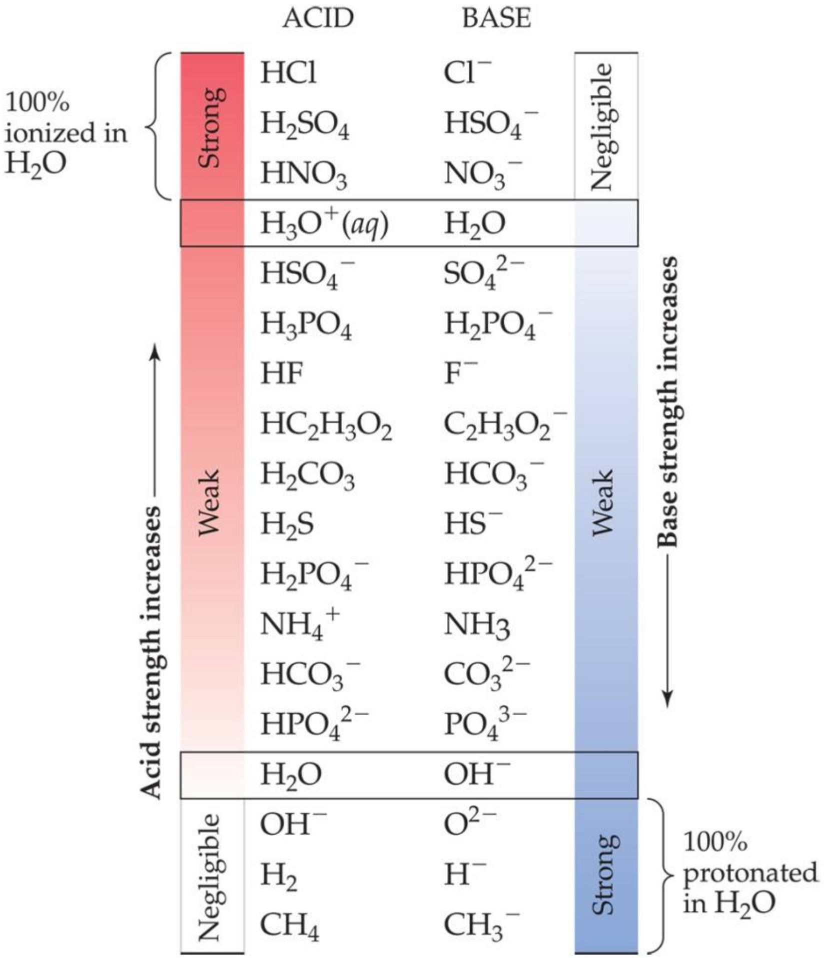
ii) combine with cations or

iii) furnish anions or electrons

$$SO_2 + Na_2O = Na_2SO_3$$

$$\underset{\text{Acid}}{Cl_2} + \underset{\text{Base}}{2Na} = 2\,NaCl$$

Acid and Base Strength



- Strong acids are completely dissociated in water.
  - Their conjugate bases are quite weak.
- Weak acids only dissociate partially in water.
  - Their conjugate bases are weak bases.
- Substances with negligible acidity do not dissociate in water.
  - Their conjugate bases are exceedingly strong.

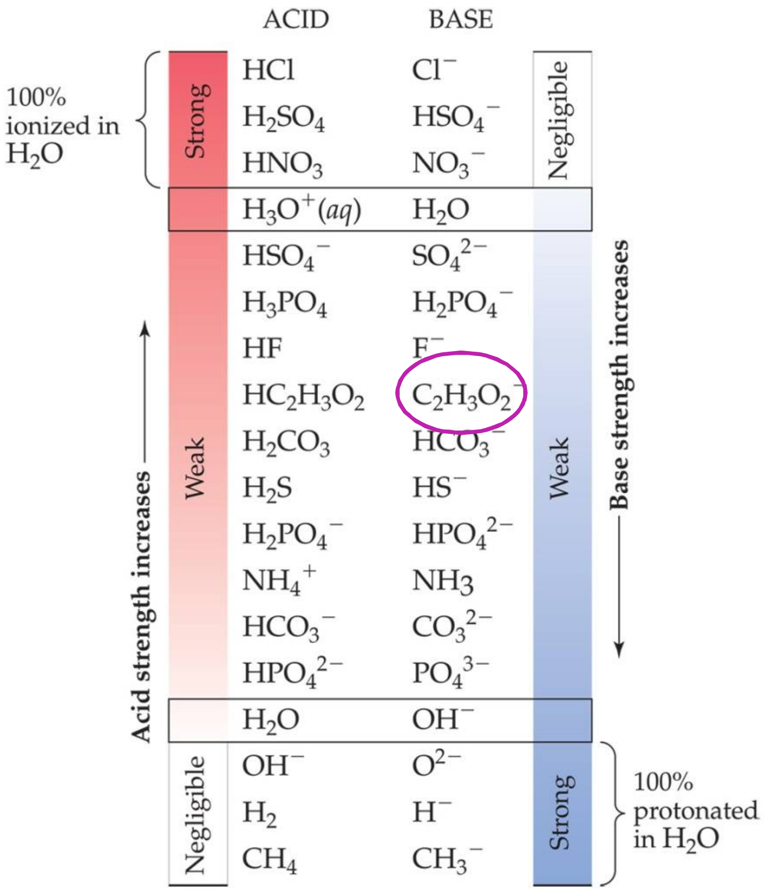
Acid and Base Strength

In any acid-base reaction, the equilibrium favors the reaction that moves the proton to the stronger base.

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

H_2O is a much stronger base than Cl^-, so the equilibrium lies so far to the right *K* is not measured ($K >> 1$).

Acid and Base Strength



Acetate is a stronger base than H_2O, so the equilibrium favors the left side (K<1).

The stronger base "wins" the proton.

$$HC_2H_3O_2(aq) + H_2O \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$$

Autoionization of Water

As we have seen, water is amphoteric.

- In pure water, a few molecules act as bases and a few act as acids.

$$H_2O(l) + H_2O(l) \rightleftharpoons OH^-(aq) + H_30^+(aq)$$

$$H_2O(l) + H_2O(l) \rightleftharpoons \left[OH^- \cdots H^+ \cdots H_20\right] \rightleftharpoons OH^-(aq) + H_30^+(aq)$$

This process is called autoionization.

Does pure water conduct electrical current?

Water is a very, very, very weak electrolyte.

$$H_2O \leftrightarrows H^+ + OH^-$$

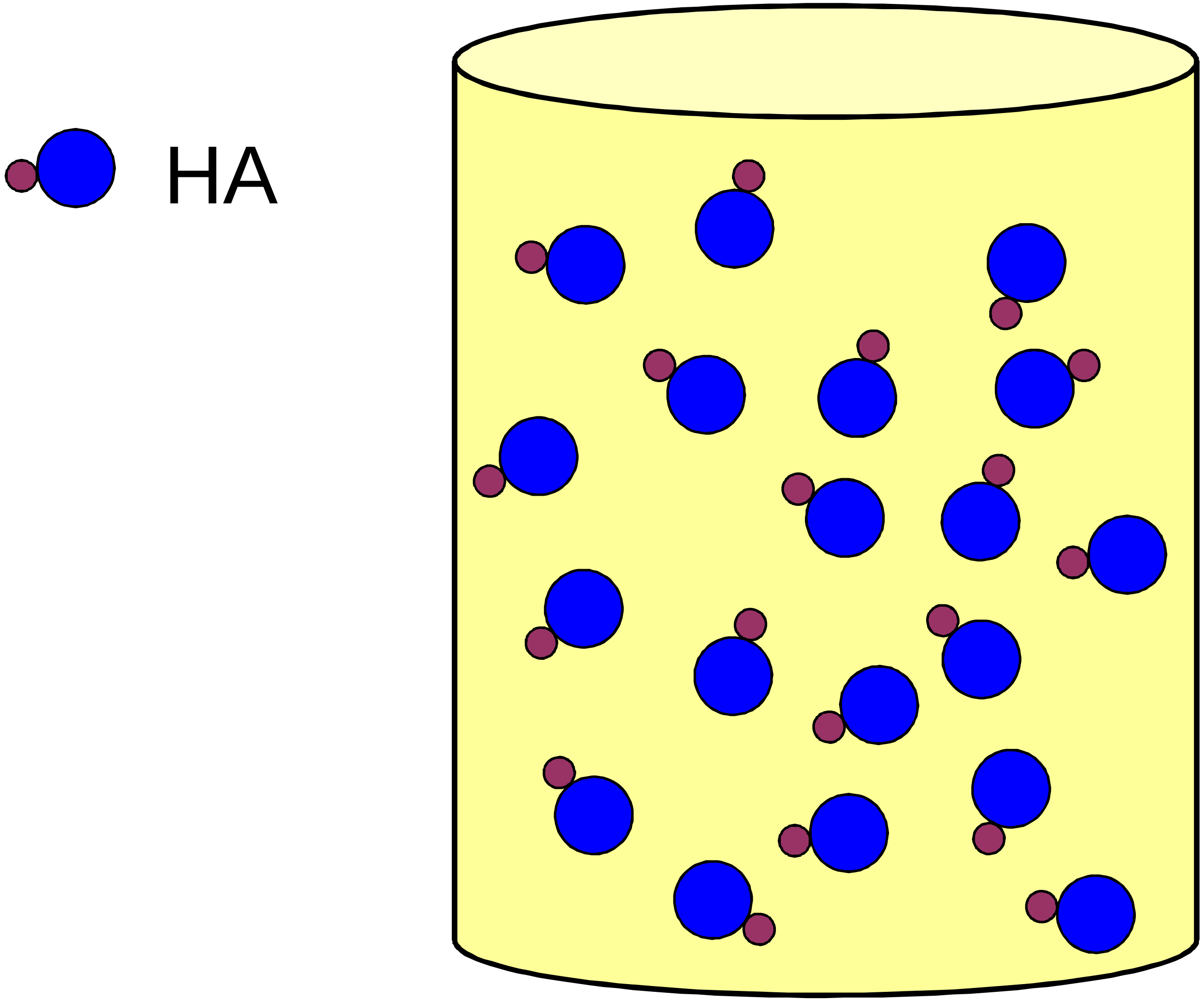
How are (H^+) and (OH^-) related?

$$(H^+)(OH^-) = 10^{-14}$$

For pure water: $(H^+) = (OH^-) = 10^{-7}M$

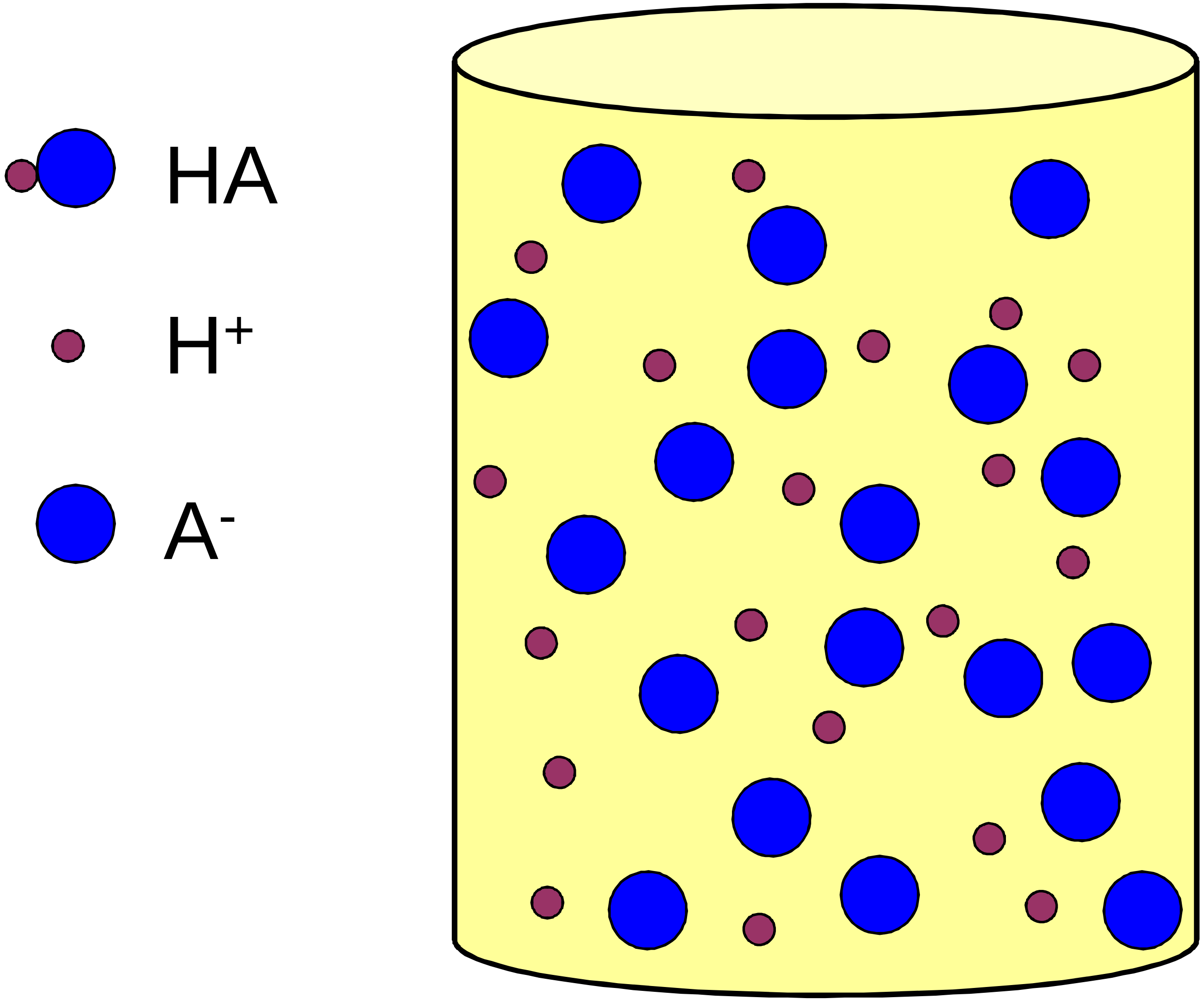
This is neutrality and
at 25^{o}C is a pH = 7.

Behavior of an acid, HA, in aqueous solution



What happens to the HA molecules in solution?

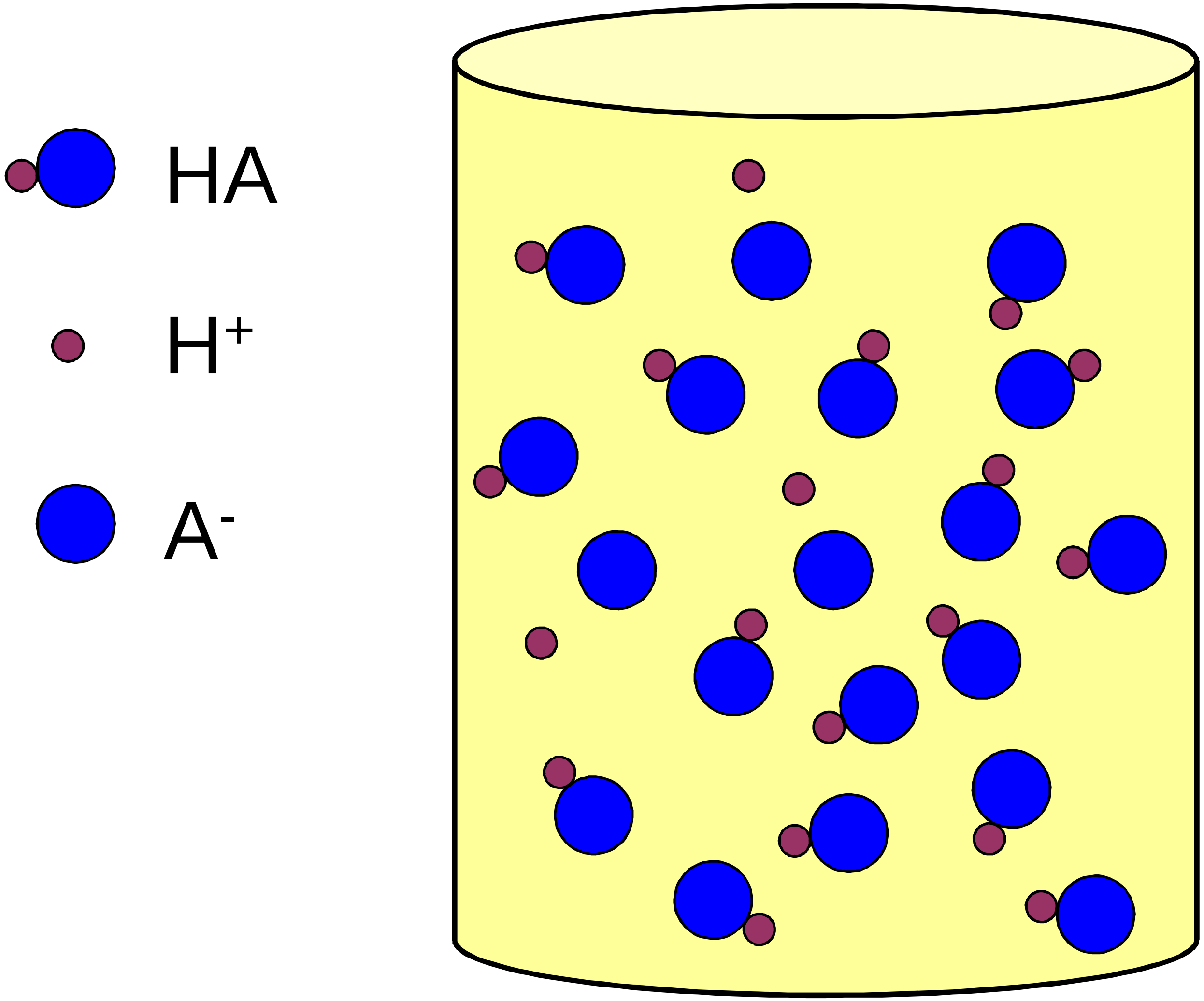
100% dissociation of HA



Strong Acid

Would the solution be conductive?

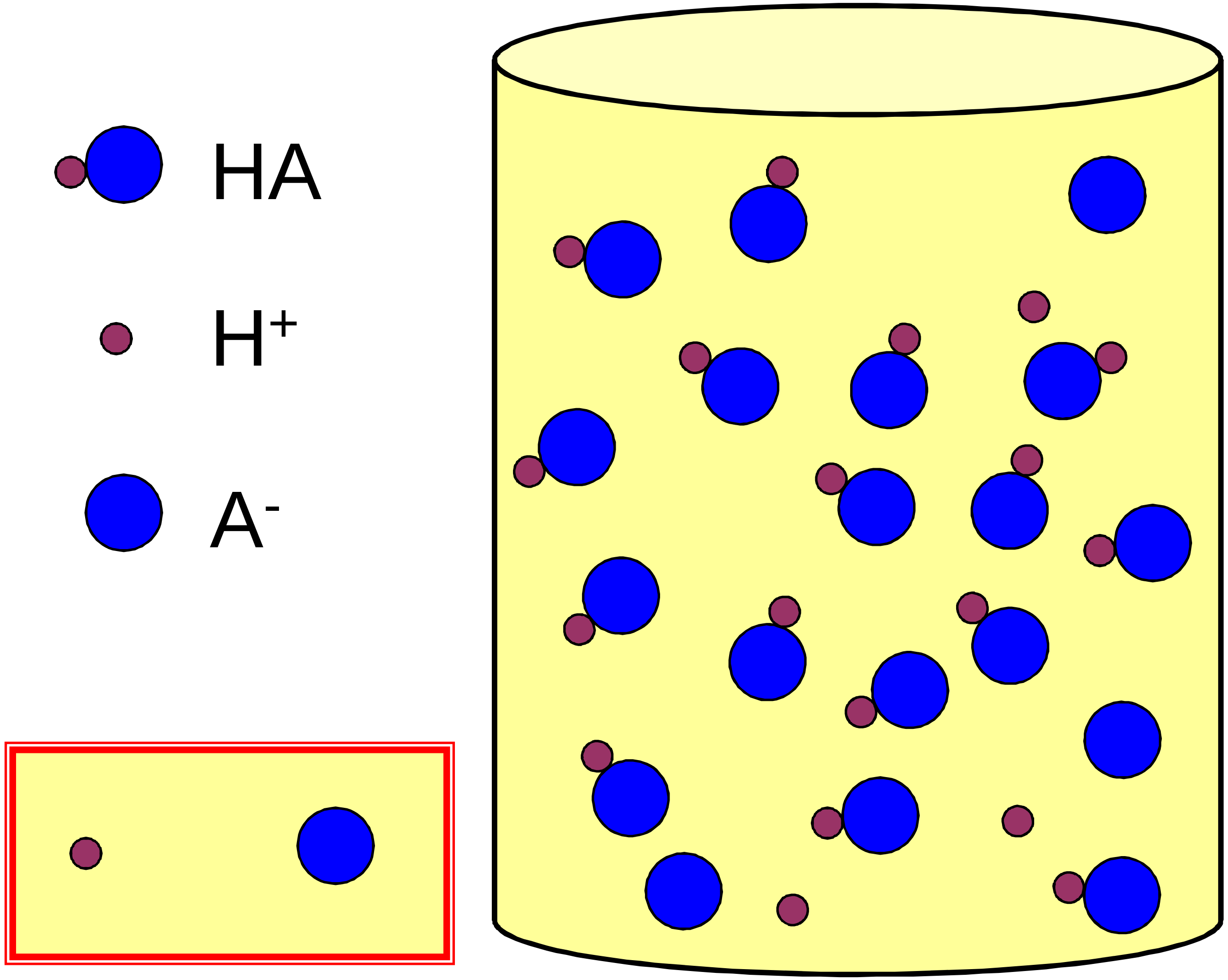
Partial dissociation of HA



Weak Acid

Would the solution be conductive?

$$HA \leftrightharpoons H^+ + A^-$$



Weak Acid

At any one time, only a fraction of the molecules are dissociated.

Strong and Weak Acids/Bases

Strong acids/bases – 100% dissociation into ions

HCl	$NaOH$
HNO_3	KOH
H_2SO_4	

Weak acids/bases – partial dissociation,
both ions and molecules

CH_3COOH	NH_3

The pH Scale

- The “p scale” is used to express small numbers. And “p” designate the power term
- $pH = -\log [H^+]$

- $H_2O + H_2O = H_3O^+ + OH^-$
- Ionic product of water: $K_w = C_{H3O+} \times C_{OH-} = 10^{-14}$
- $-\log K_w = -\log C_{H3O+} . C_{OH-} = -\log C_{H3O+} - \log C_{OH-}$ or $pK_w = pH + pOH$
- $pH + pOH = 14$

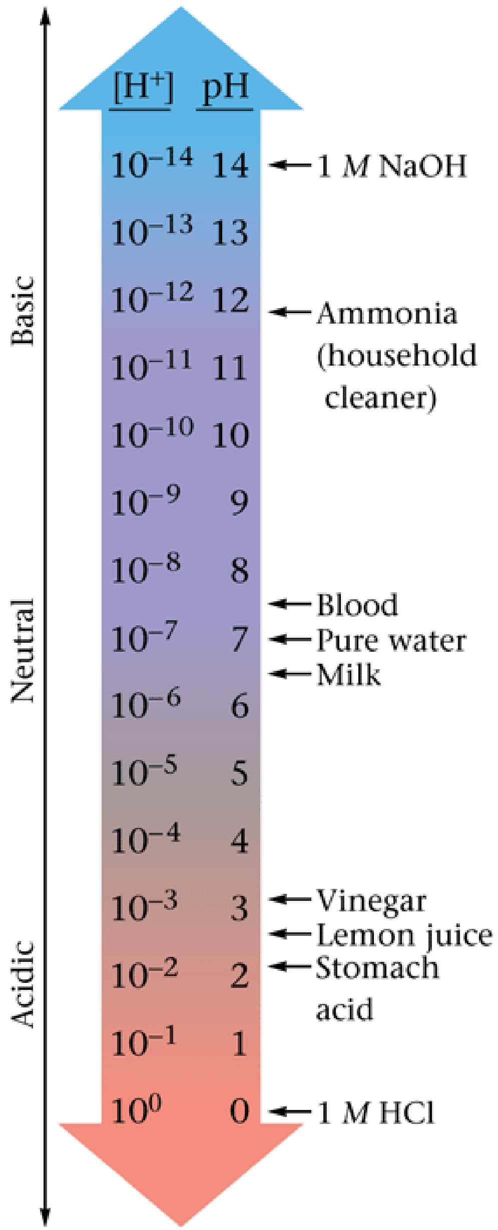
The pH Scale

The Relationship of the H^+ Concentration of a Solution to Its pH

$[H^+]$	pH
1.0×10^{-1}	1.00
1.0×10^{-2}	2.00
1.0×10^{-3}	3.00
1.0×10^{-4}	4.00
1.0×10^{-5}	5.00
1.0×10^{-6}	6.00
1.0×10^{-7}	7.00

pH scale is a log scale based on 10, the pH changes by 1 for every power of 10 change in the $[H^+]$.

The pH Scale

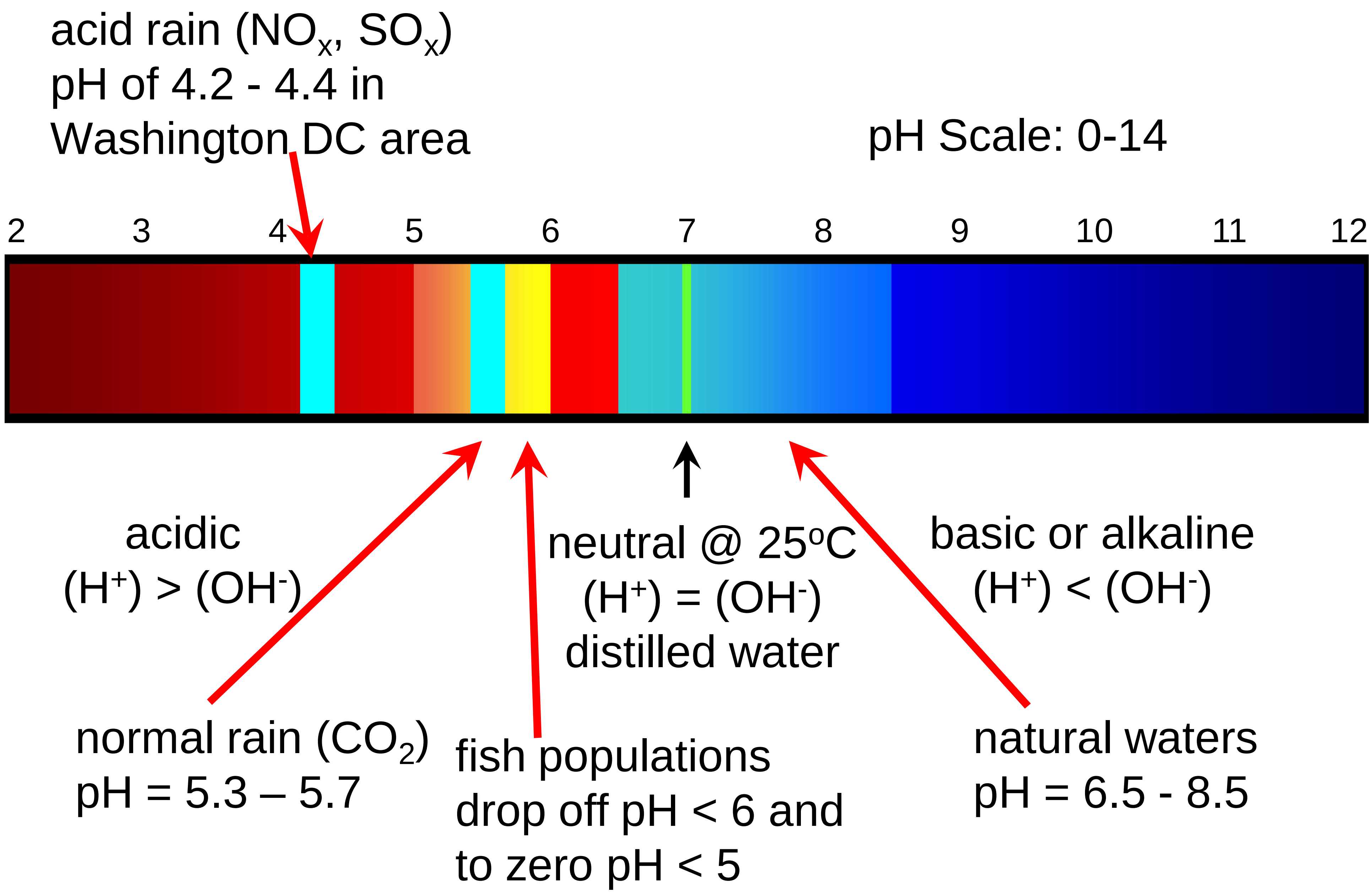


How Do We Measure pH?

pH meter

pH paper change to different colors to different pH ranges for rough estimation

Acid Rain and pH



Factors Affecting Acid Strength

	GROUP			
	4A	5A	6A	7A
Period 2	CH_4 No acid or base properties	NH_3 Weak base	H_2O –––	HF Weak acid
Period 3	SiH_4 No acid or base properties	PH_3 Weak base	H_2S Weak acid	HCl Strong acid

Increasing acid strength

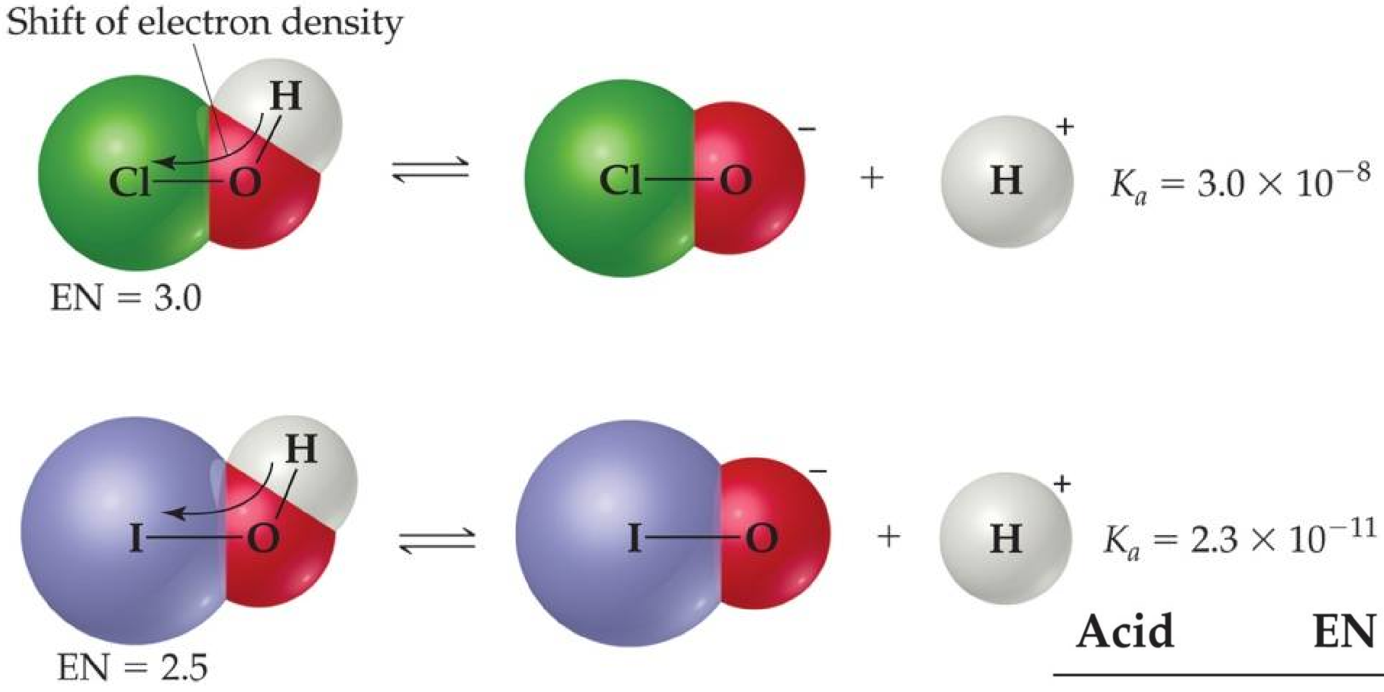
Increasing base strength

Increasing acid strength

Increasing base strength

- The more polar the H-X bond and/or the weaker the H-X bond, the more acidic the compound.
- Acidity increases from left to right across a row and from top to bottom down a group.

Factors Affecting Acid Strength

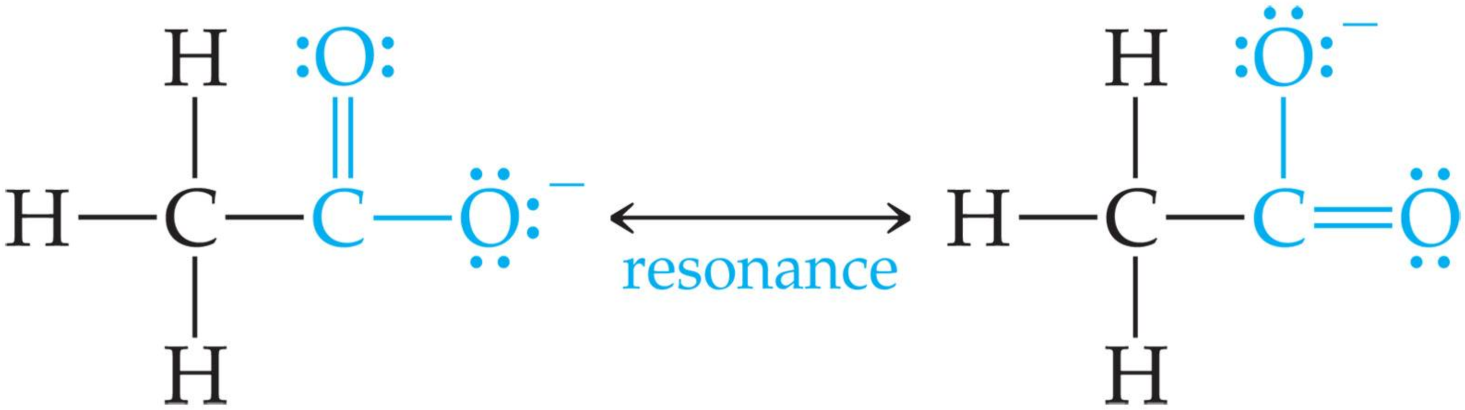


Acid	EN of Y	K_a
HClO	3.0	3.0×10^{-8}
HBrO	2.8	2.5×10^{-9}
HIO	2.5	2.3×10^{-11}

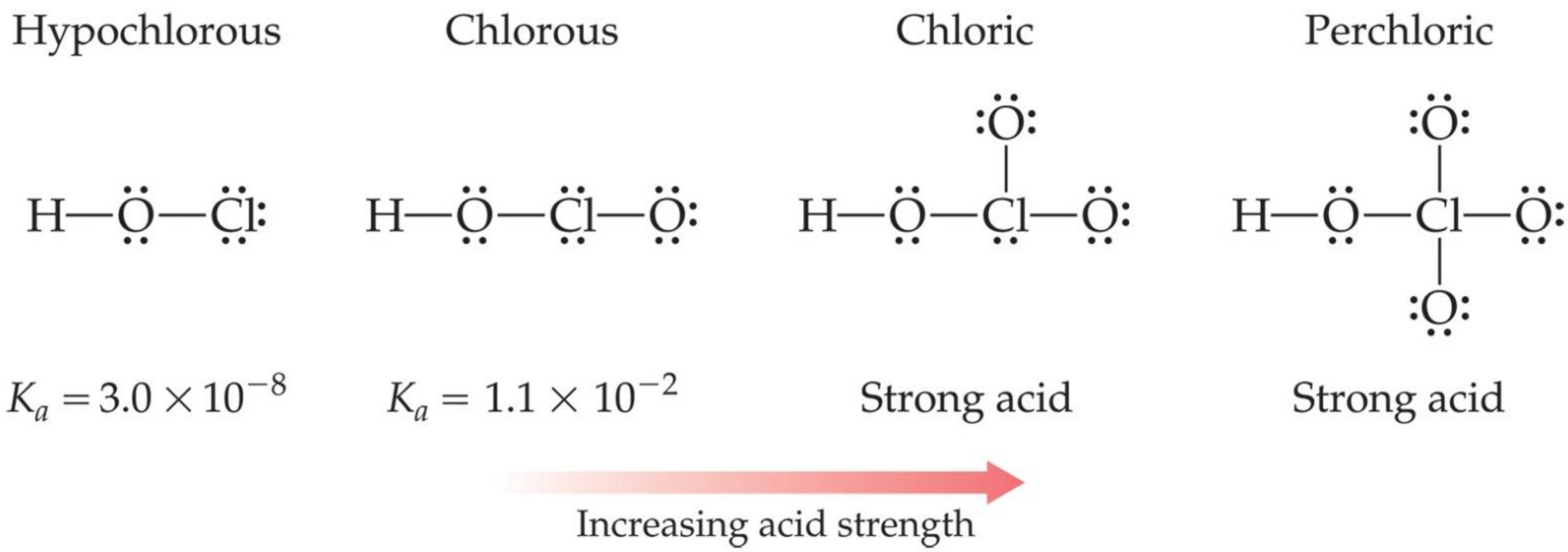
In oxyacids, in which an OH is bonded to another atom, Y, the more electronegative Y is, the more acidic the acid.

Factors Affecting Acid Strength

Resonance in the conjugate bases of carboxylic acids stabilizes the base and makes the conjugate acid more acidic.



Factors Affecting Acid Strength



Anything that effects the polarity of the O-H bond will affect the strength of the acid

- An increase in the electronegativity of an atom bound to “O” increases in polarity of the bond and makes it more acidic
- More oxygen = more polar

Pauling Scale for pH measurement

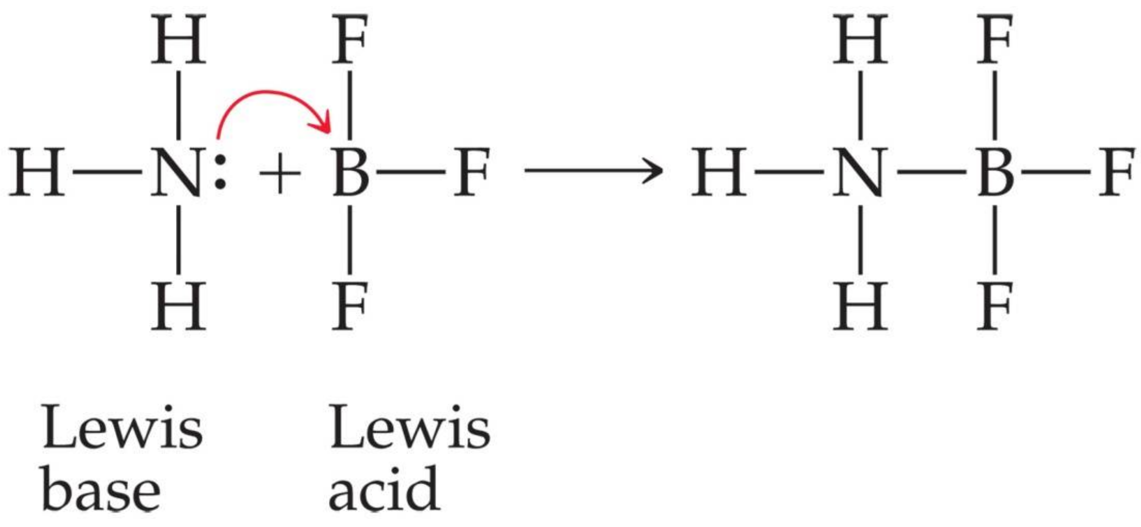
First rule: For an oxyacid of the type $O_nX(OH)_m$, $pK_a \approx 8-5n$ i.e. the acid strength depends upon the number of non hydrogenated oxygen atom.

Second rule: For polyprotic acid(m>1), the successive pKa values increase by 5 units.

Value of n	Value of pK_a	Oxoacid (Observed pK_a)
0	8	HOCl (7.2)
1	pK_1= 3	H_2CO_3 (3.6)
	pK_2=8	
	pK_3=13	H_3PO_4 (2.1, 7.4, 12.7)
2	-2	HNO_3 (1.4)

The pK_a of HIO_6 is 3.29, and this seems high, but if one looks at the structure, we see that it is $(HO)_5IO$, and so n=1 and the pK_a is predicted to be 3. The rule is therefore fairly accurate, and can also be used as a tool for predicting the structure.

Lewis Acids



- Lewis acids are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.
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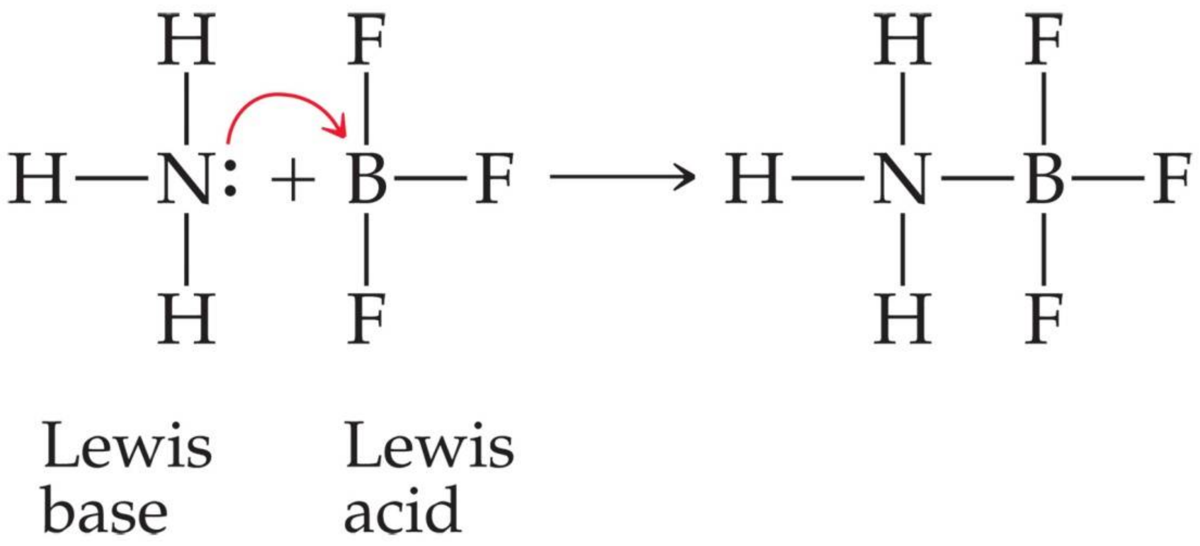
Lewis Bases



- Lewis bases are defined as electron-pair donors.
- Anything that is a Brønsted–Lowry base is also a Lewis base. (B-L bases also have a lone pair.)
- Lewis bases can interact with things other than protons.

Lewis Acids and Bases

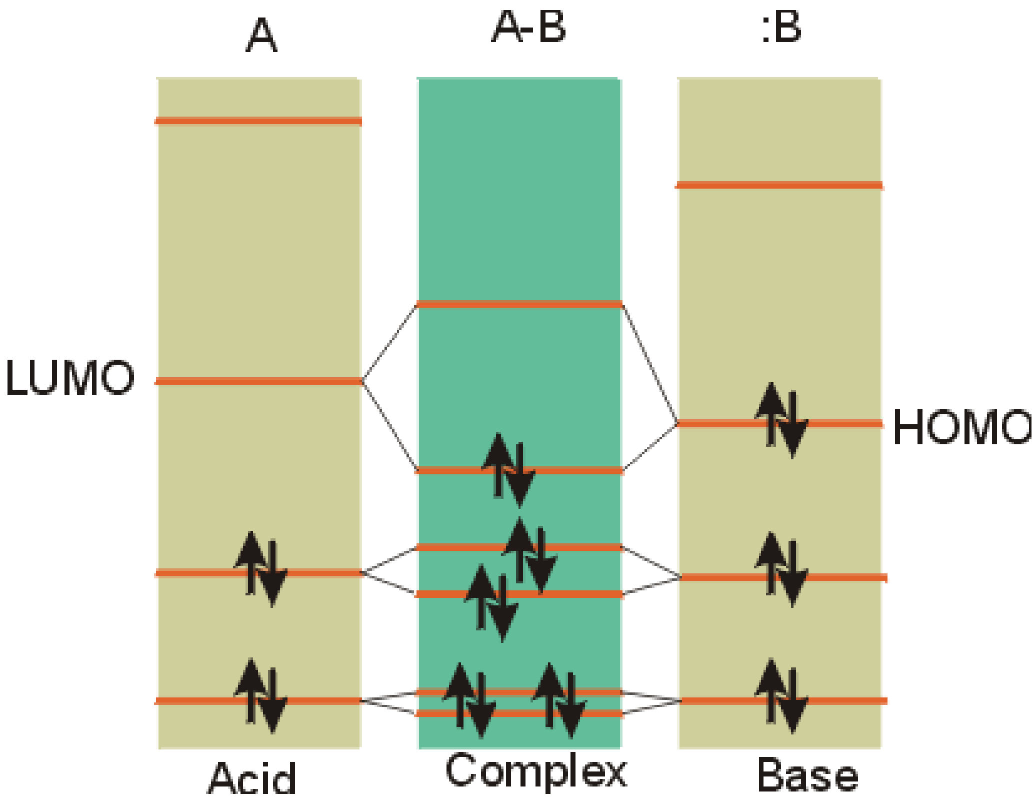
Electron-deficient compounds such as trivalent boron is categorized as a Lewis acid.

$$B(CH_3)_3 + :NH_3 \rightarrow \quad (CH_3)_3B \leftarrow NH_3$$

The HOMO on the Lewis base interacts with the electron pair in the LUMO of the Lewis acid. The MOs of the adduct are lower in energy.

A Lewis base has an electron pair in its highest occupied molecular orbital (HOMO) of suitable symmetry to interact with the LUMO of the Lewis acid. The closer the two orbitals are in energy, the stronger the bond in the adduct.

Lewis Acids and Bases

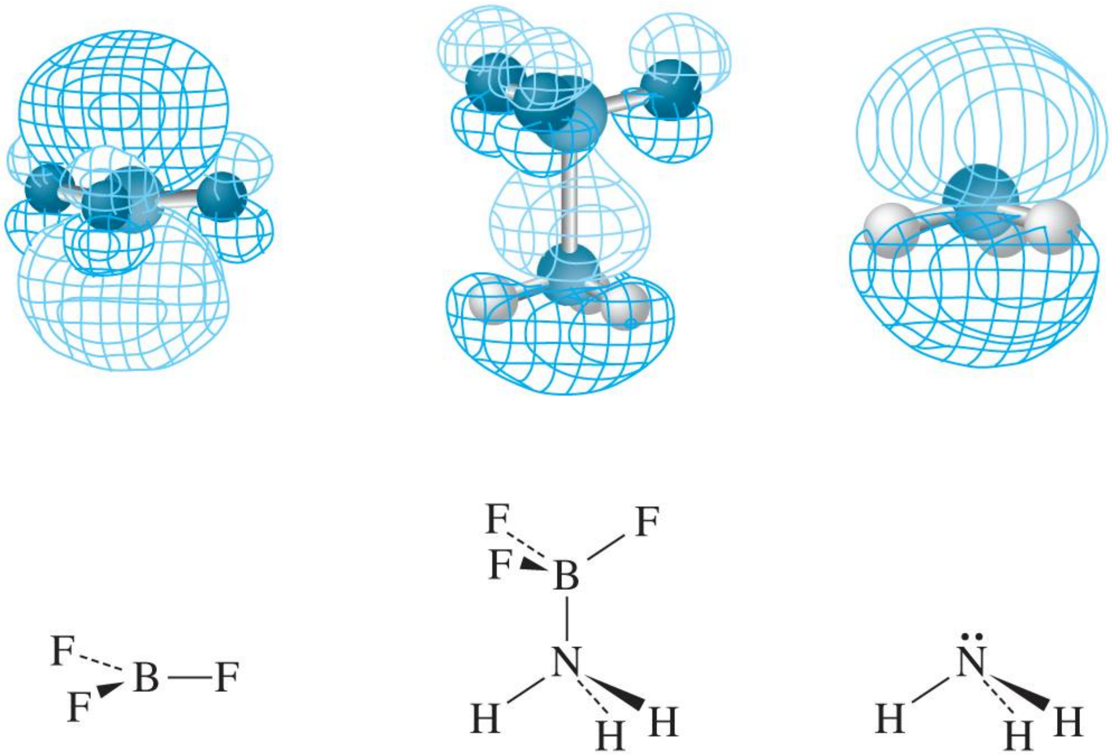


The LUMO and HOMO are called *frontier orbitals*.

If there is a net lowering of energy, the adduct is stable.

Adduct of $BF_3 + NH_3$

The LUMO of the acid, the HOMO of the base and the adduct are shown below:



HSAB Concept

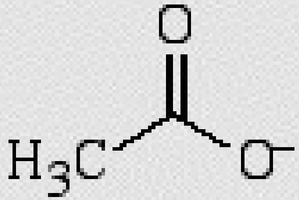
Pearson classified Lewis acids and Lewis bases as
hard, ***borderline*** or ***soft***.
According to Pearson's *hard soft* [Lewis] acid base (HSAB) principle:
***Hard* [Lewis] acids prefer to bind to *hard* [Lewis] bases**
and
***Soft* [Lewis] acids prefer to bind to *soft* [Lewis] bases**

However, Pearson classified a very wide range of
atoms,
ions,
molecules and
molecular ions
as ***hard, borderline or soft* Lewis acids or Lewis bases,**

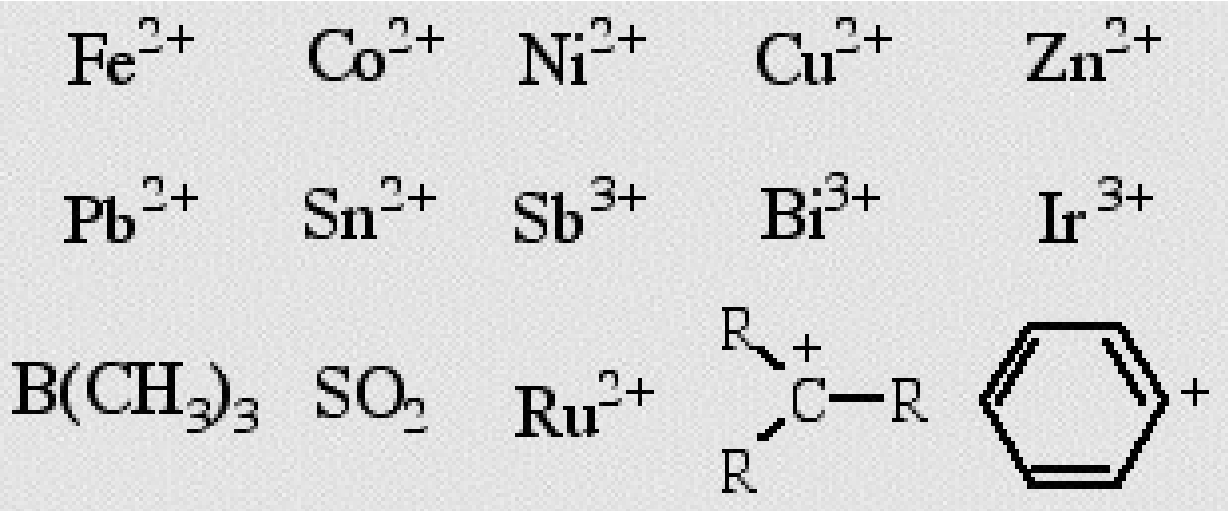
Hard Acids

H^+	Na^+	K^+	Be^{2+}	Mg^{2+}
Ca^{2+}	Mo^{3+}	Mn^{2+}	Al^{3+}	Sc^{3+}
In^{3+}	Cr^{3+}	Co^{3+}	Fe^{3+}	Ti^{4+}
Zr^{4+}	U^{4+}	Ce^{3+}	Sn^{4+}	BF_3
$AlCl_3$	AlH_3	SO_3	NO_2^+	CO_2

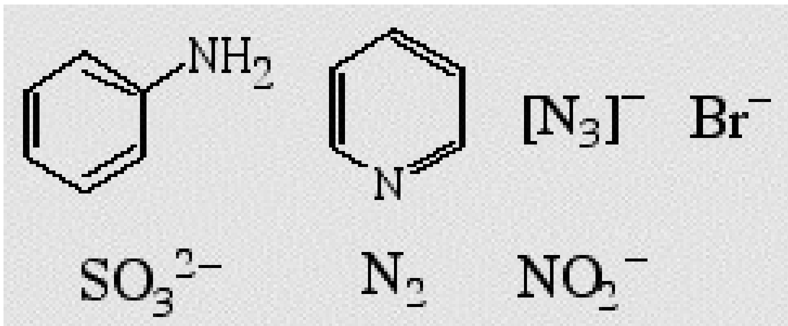
Hard Bases

H_2O	HO^-	F^-		PO_4^{3-}
SO_4^{2-}	Cl^-	CO_3^{2-}	ClO_4^-	NO_3^-
R-OH		H_3N	$R-NH_2$	H_2N-NH_2

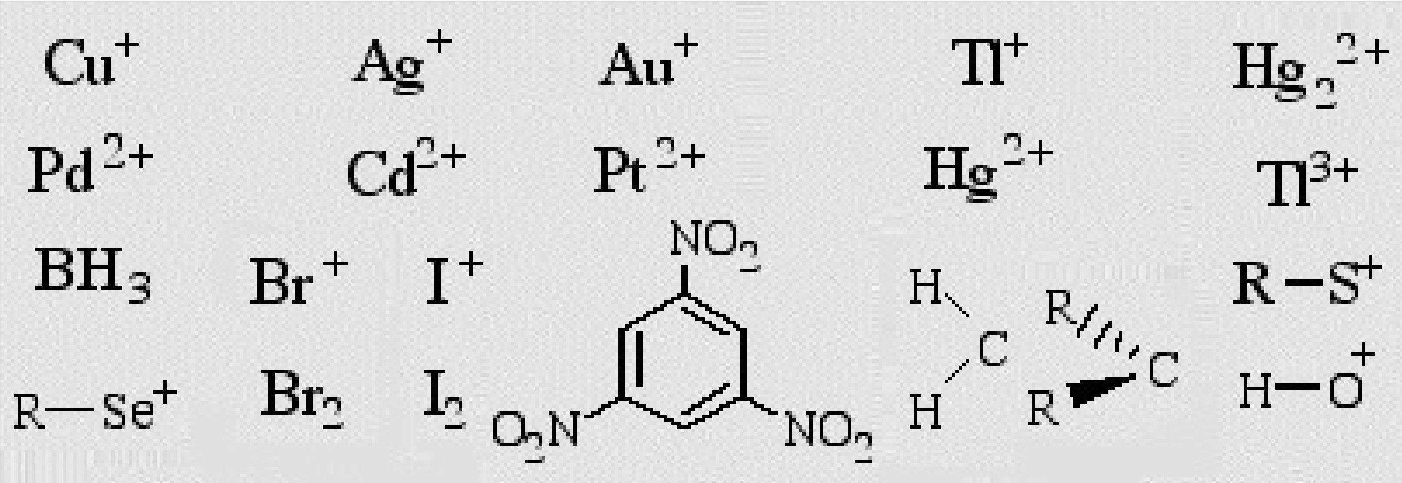
Borderline Acids



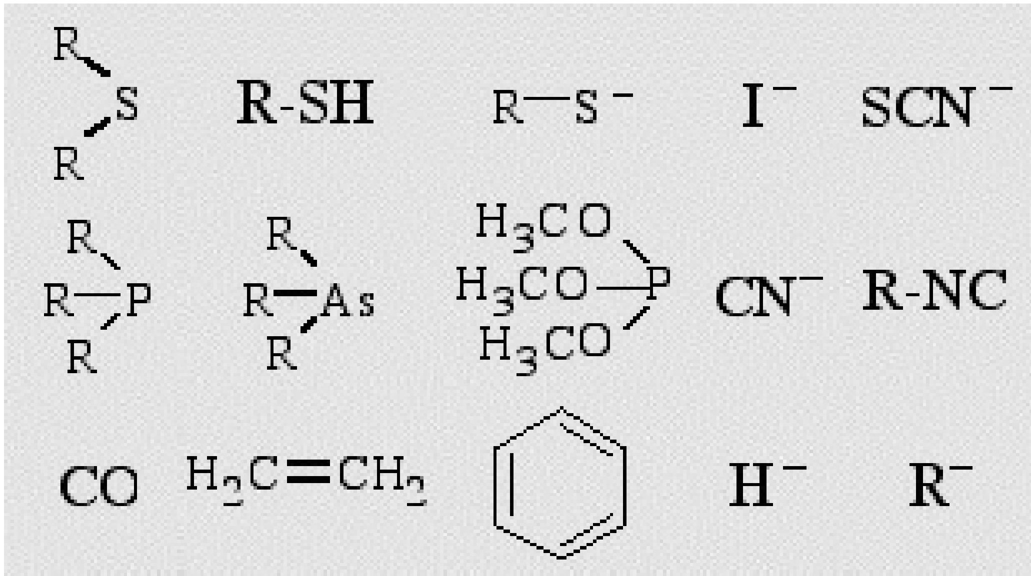
Borderline Bases



Soft Acids



Soft Bases



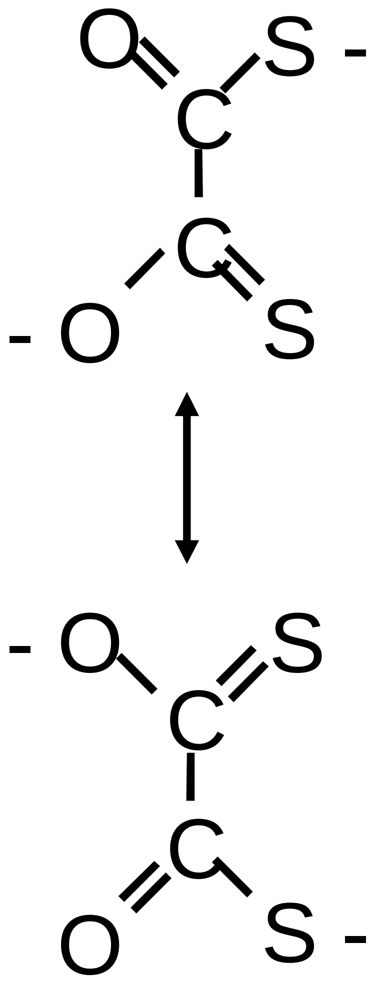
Hard and Soft Acids

	Hard Acid	Soft Acid
	Acceptor atom marked by	Acceptor atom marked by
1	Small size	Large size
2	High positive oxidation state	Zero or low positive oxidation state
3	Absence of any outer electrons which are easily excited to higher states	Presence of several easily excitable valency electrons
4	Example:H^+, Li^+, Fe^{3+}, $AlCl_3$ etc	Example: Cu^+, Hg^+, I_2, Pd^{2+} etc

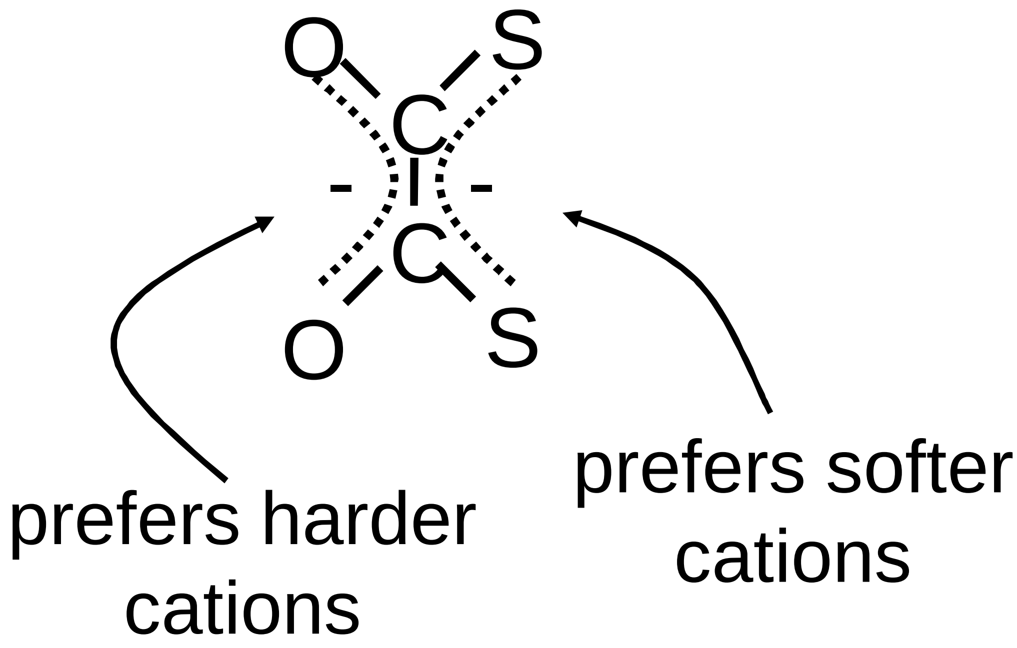
Hard and Soft Bases

	Hard Base	Soft Base
	Donor atom marked by	Donor atom marked by
1	High electronegativity	Low electronegativity
2	Low polarisability	High polarisability
3	Presence of filled orbital, empty orbitals may exist at higher energy level	Partially filled orbitals, empty orbitals are low lying.
4	Example: OH^-, F^-, CO_3^{2-}, NH_3 etc	Example: H^-, I^-, CO, RS^- etc

Hard and Soft Acids and Basesc



Dithiooxalate ion
can chelate on two sides.



Hard and Soft Acids and Basesc

Dithiooxalate ion
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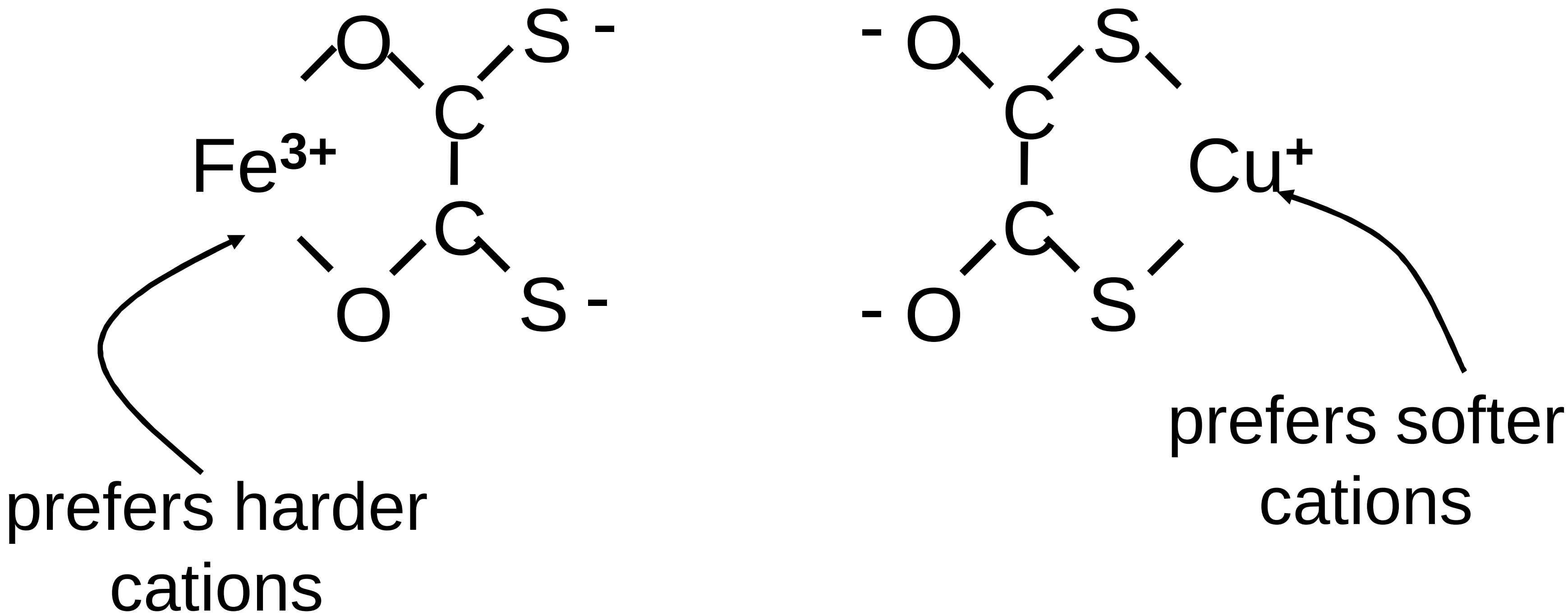


Hard acids tend to react better with hard bases
and soft acids with soft bases, in order to
produce hard-hard or soft-soft combinations

In general, hard-hard combinations are
energetically
more favorable than soft-soft

**An acid or a base may be hard or soft
and at the same time it may be strong or weak**

Hammett acidity function, H_0

H_o (Hammett acidity function) is used to define acidity of concentrated solutions (or strong acids)

This function can be conveniently estimated with reference to known bases (indicators).

Hammett acidity function

For the reaction,

$B + H^+ \leftrightarrows BH^+$; $K_B = [BH^+] / [B] [H]$ (in dilute solutions);

Hammett acidity, $h_o = [H] = (1/ K_B)[BH^+]/[B]$

H_o (Hammett acidity function) $= - \log h_o = \log K_B - \log [BH^+]/[B]$

$H_o = - pK_B + \log [B]/[BH^+]$

pK_B and $[B]/[BH^+]$ are obtained experimentally and H_o calculated

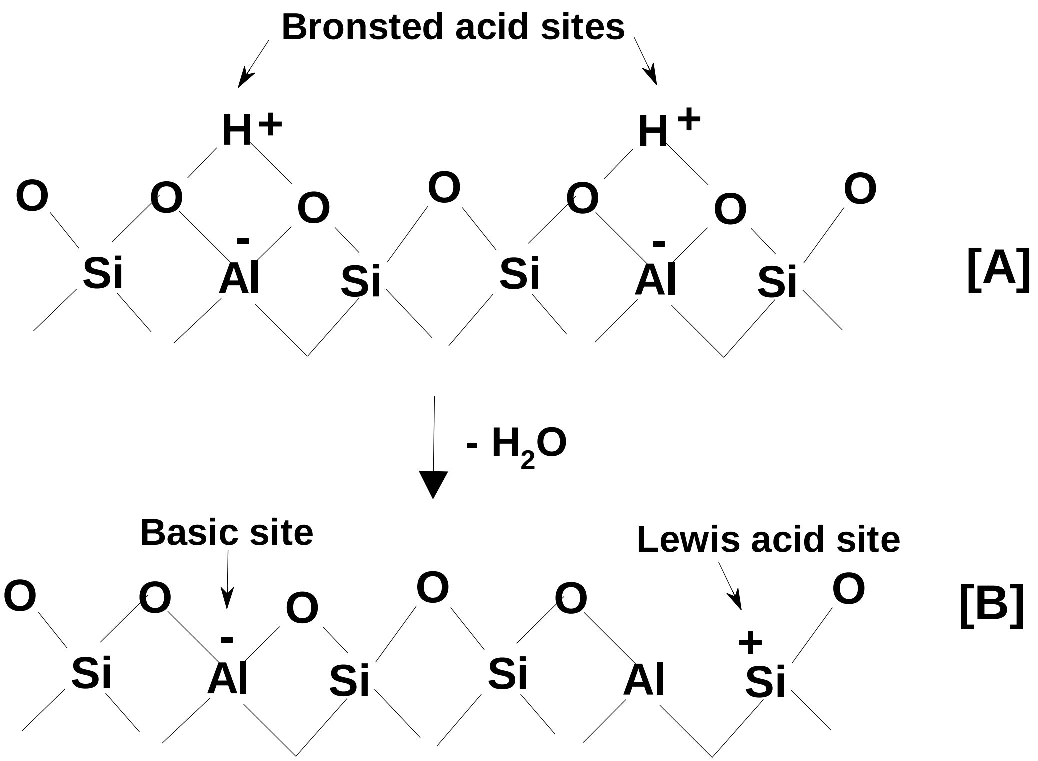
In dilute solutions, H_o = pH;
in conc. solutions, it is $H_o = pH - \log (f_B/f_{BH+})$

Typical Hammett acidity (H_o) of some strong acids used in catalysis

Acid	H_o[a]
Conc. H_2SO_4	~ -12
Anhydrous HF	~ -10
SiO_2-Al_2O_3	- 8.2 - 10
SiO_2-MgO	< + 1.5
SbF_5- Al_2O_3	< -13.2
Zeolite, H-ZSM-5	-8.2 - 13
Zeolite, RE-H-Y	-8.2 - 13

[a] : Denotes the strength of the strongest acid sites in solid acids

In zeolites and silica-alumina Brönsted acid sites Transform into Lewis acid sites on heating



SOLID ACID CATALYSTS

Examples:

- Zeolites
- SAPOs
- Clays; pillared clays
- Ion-exchange resins
- Oxides; SO_4-oxides
- Mixed oxides; amorphous
- Heteropoly acids

Solid bases

- **Alkali and alkaline earth oxides;**
- **RE-oxides; ThO_2;**
- **Alkaline-zeolites;**
- **Alkali metals or oxides on Al_2O_3 and SiO_2;**
- **Hydrotalcite; Sepiolite**

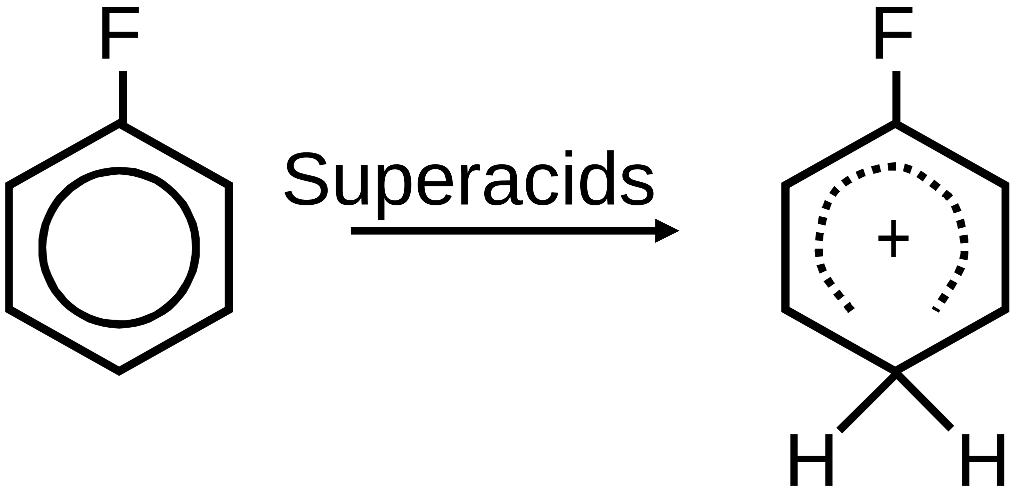
Activity depends on concentration and strength of basic sites
Basicity may be measured by adsorption of acids
Often involve carbanion intermediates

Superacids

More acidic than concentrated sulfuric acid.

Capable of protonating compounds that don't want to be protonated.

Causing isomerization in the most unlikely candidates.



$$(CH_3)_3COH \xrightarrow{\text{Superacids}} (CH_3)_3C^+ + H_3O^+$$

$$I_2 \xrightarrow{\text{Superacids}} I_2^+ \text{ and/or } I_3^+$$

Superacids

Acids which are stronger than pure sulfuric acid.

$$BH^+ \leftrightarrows B + H^+ \qquad pK_{BH^+}$$

Super acids are measured with the Hammett acidity function (H_o)

$$H_o = pK_{BH^+} - \log \frac{[BH^+]}{[B]}$$

Hammett acidity is determined Spectro-photometrically by determining $[BH^+]$ and [B]

B is an indicator base. e.g.,nitroaniline, benzene, picramide

Superacids acidity

		H_o
hydrofluoric acid	HF	-11.0
100% sulfuric acid	H_2SO_4	-11.9
perchloric acid	$HClO_4$	-13.0
fluorosulfuric acid	HSO_3F	-15.6
triflic acid (trifluoromethanesulfonic acid)	HSO_3CF_3	-14.6
magic acid™	$HSO_3F\text{-}SbF_5$	-21 to -25
fluoroantimonic acid	$HF\text{-}SbF_5$	-21 to -28

Measured in non-aqueous systems

$$(C_6H_5)_3COH + \text{superacid} \rightarrow (C_6H_5)_3C^+ + H_3O^+$$

trivalent carbocation
(carbenium ion)

$$\text{alkyl-Cl} + \text{superacid} \rightarrow \text{alkyl}^+ + \text{HCl}$$

$$\text{hydrocarbon} + \text{superacid} \rightarrow \text{hydrocarbon-H}^+$$

pentacoordinate carbocation
(carbonium ion)

George Olah 1994 Nobel Prize

Superacids

Formed by mixing

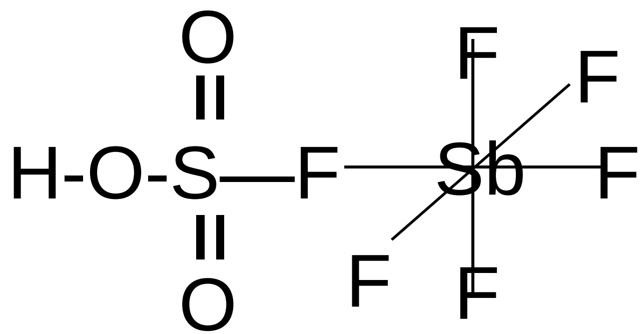
fluorine containing Bronsted acid or metal oxide + fluorinated Lewis acid

HF, HSO_3F, HSO_3CF_3

TiO_2, SiO_2

BF_3, SbF_5, TaF_5

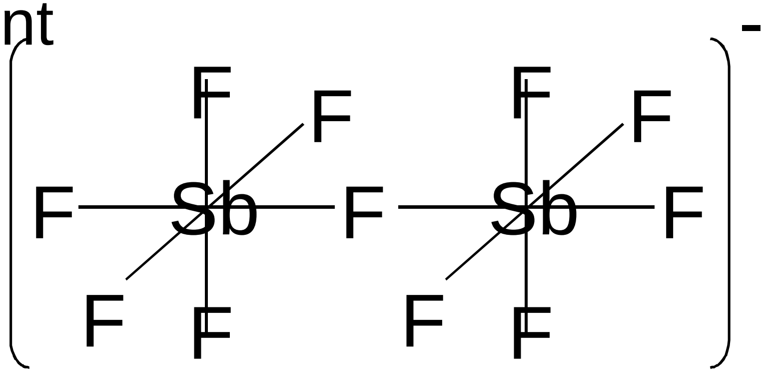
Superacids

$HSO_3F + SbF_5 \rightarrow$ 

fluorosulfonic acid

antimony pentafluoride complexing agent

magic acid™

$2\ HF + 2\ SbF_5 \rightarrow H_2F^+ +$ 

fluoroantimonic acid

Why are superacids so acidic? As the conjugate base of the acid is more stable due to delocalization of charge, so the acid is highly acidic in nature

Drago-wayland equation

$$A(g) + :B(g) \rightarrow A\text{---}B(g)$$

$$-\Delta H = E_A E_B + C_A C_B$$

E parameters characterising the acid and base are related to the susceptibility of the species to undergo electrostatic interaction;

the C parameters represent the susceptibility to form covalent bonds

End