

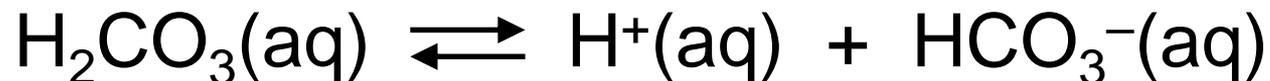
Polyprotic acids – like sulfurous acid, H_2SO_3 – have more than one ionizable H.



so K_a values \downarrow w/each H^+ removed.

-- Usually, K_{a2} is at least 1000X smaller than K_{a1} . In such cases, one can calculate $[\text{H}^+]$ and pH based only on K_{a1} (i.e., ignore K_{a2} and pretend you have a monoprotic acid).

Find the pH of a 0.0037 M carbonic acid solution.
($K_{a1} = 4.3 \times 10^{-7}$, $K_{a2} = 5.6 \times 10^{-11}$)



at eq. [] 0.0037 - x x x

$$4.3 \times 10^{-7} = \frac{x^2}{0.0037 - x} \quad \xrightarrow{\text{shortcut}} \quad 4.3 \times 10^{-7} = \frac{x^2}{0.0037}$$

$$x = [\text{H}^+] = 3.97 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.40$$

$$x = [\text{H}^+] = 3.99 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.40$$

([H⁺] after 1st ionization = 3.97 x 10⁻⁵ M)



at eq. []

$$3.97 \times 10^{-5} - y \qquad 3.97 \times 10^{-5} + y \qquad y$$

$$5.6 \times 10^{-11} = \frac{(3.97 \times 10^{-5} + y)(y)}{3.97 \times 10^{-5} - y}$$

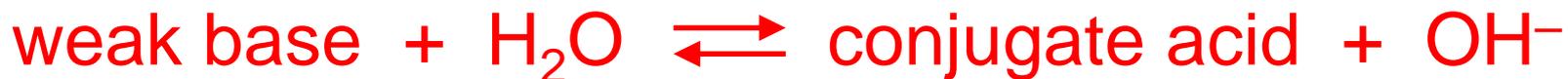
$$5.6 \times 10^{-11} = \frac{(3.97 \times 10^{-5}y + y^2)}{3.97 \times 10^{-5} - y}$$

$$y = \text{add'l } [\text{H}^+] = 5.6 \times 10^{-11} \text{ M}$$

 totally
negligible

$$\text{pH} = 4.40$$

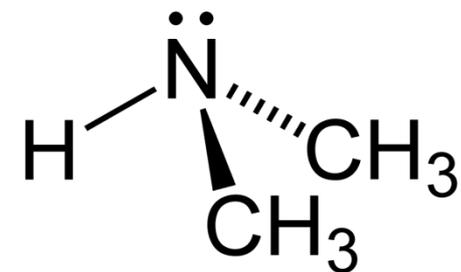
Weak Bases (i.e.,



$$K_b = \frac{[\text{conj. acid}] [\text{OH}^-]}{[\text{weak base}]}$$

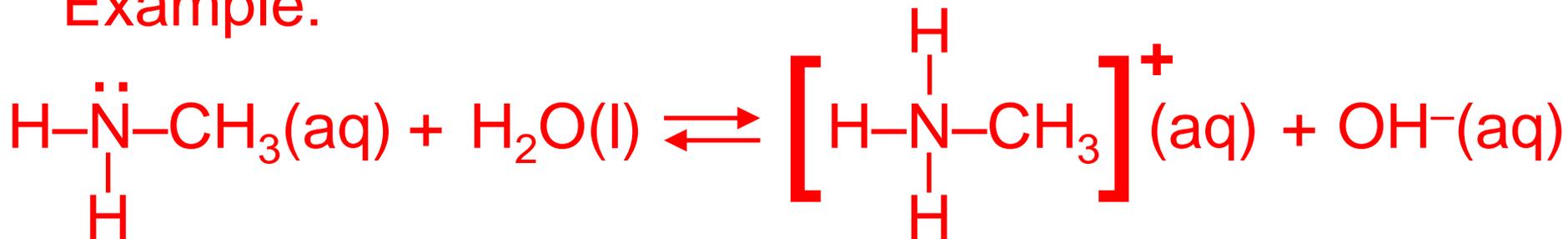
Weak bases are often nitrogen-containing molecules (“amines”) or anions.

(all of these have lone e⁻ pairs)



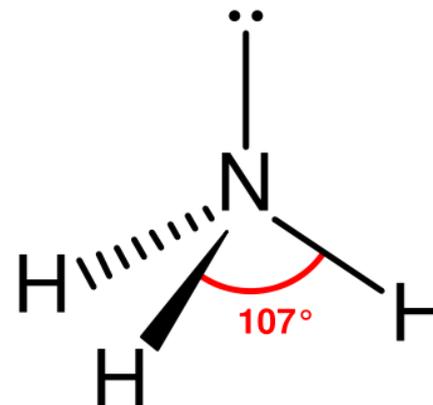
dimethylamine

Example:



What is the conc. of ammonia
in a solution of pH 9.35?

Ammonia's $K_b = 1.8 \times 10^{-5}$.

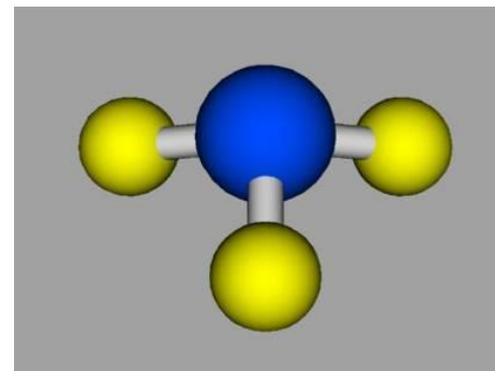


Since $\text{pOH} = 4.65$, $[\text{OH}^-] =$



$$1.8 \times 10^{-5} = \frac{(2.24 \times 10^{-5})^2}{x - 2.24 \times 10^{-5}}$$

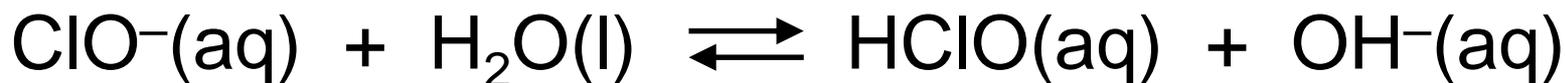
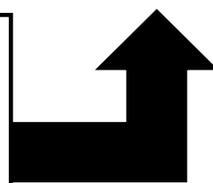
$$x = [\text{NH}_3]_{\text{init.}} = 5.0 \times 10^{-5} \text{ M}$$



Anions related to Weak Acids



This is the conj. base of HClO, so it acts as a weak base in H₂O (i.e., it accepts H⁺).

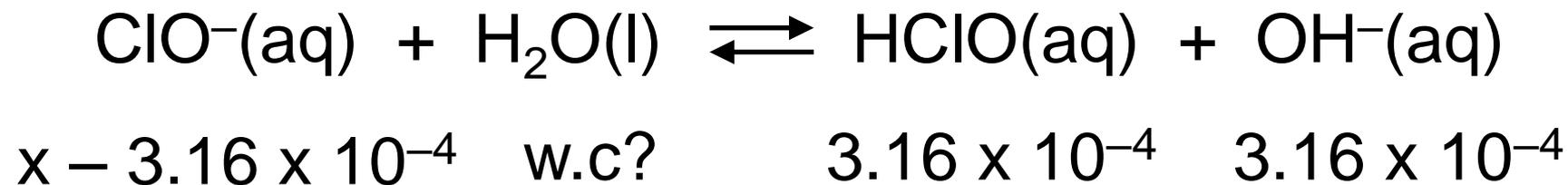


Sodium hypochlorite is the active ingredient in bleach, which is used as a laundry additive and to disinfect water for swimming pools.



What mass of NaClO is required to make 2.0 L of a pH 10.50 solution? The K_b for ClO^- is 3.3×10^{-7} .

Since $\text{pOH} = 3.50$, $[\text{OH}^-] =$



$$K_b = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-]}$$

$$3.3 \times 10^{-7} = \frac{(3.16 \times 10^{-4})^2}{x - 3.16 \times 10^{-4}}$$

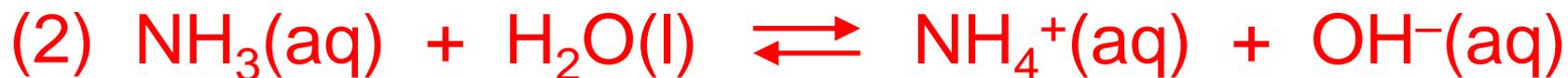
$x =$

$$\begin{array}{l} \text{M NaClO} = \frac{\text{mol NaClO}}{\text{L soln}} \\ \downarrow \qquad \qquad \qquad \searrow \\ 0.3029 \text{ M} \qquad \qquad \qquad 2.0 \text{ L} \end{array}$$

0.6058 mol NaClO

45 g NaClO

Relationship Between K_a and K_b



$$K_a =$$

$$K_b =$$

$$\text{Then } K_a \times K_b = \frac{[\text{NH}_3][\text{H}^+][\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4^+][\text{NH}_3]} = [\text{H}^+][\text{OH}^-]$$

For an acid and its conj. base:

$$K_a K_b = K_w = 1.00 \times 10^{-14}$$

Because they are easily calculated from K_a values, reference tables are often “short” on K_b values.

Just like $\text{pH} = -\log [\text{H}^+]$,

If $[\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14}$

and $\text{pH} + \text{pOH} = 14$

then since $K_a K_b = 1.00 \times 10^{-14}$

$$\text{p}K_a + \text{p}K_b = 14 \quad (@ 25^\circ\text{C})$$

$$\text{p}K_a = -\log K_a$$

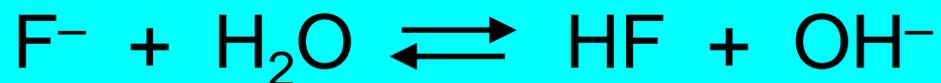
$$\text{p}K_b = -\log K_b$$

For hydrofluoric acid, $K_a = 6.8 \times 10^{-4}$.

a. Write the formula of the conjugate base.



b. Write the equation for which K_b applies.



c. Write the equation for which K_a applies.



d. Find $\text{p}K_a$, $\text{p}K_b$, and K_b .

$$\text{p}K_a = -\log K_a = -\log (6.8 \times 10^{-4}) \longrightarrow \text{p}K_a = 3.17$$

$$3.17 + \text{p}K_b = 14 \longrightarrow \text{p}K_b = 10.83$$

$$(6.8 \times 10^{-4}) K_b = 1 \times 10^{-14} \longrightarrow K_b = 1.5 \times 10^{-11}$$

Acid-Base Properties of Salt Solutions

Because ions can exhibit acid or base properties (i.e., donate or accept protons), salt solutions can be acidic or basic.

-- hydrolysis: occurs when ions “react” w/ H_2O ; the H_2O is split into H^+ and OH^-

Hydrolysis occurs when the acetate ion in sodium acetate reacts with water to produce acetic acid and hydroxide ion.



Anions of weak acids react with water to form OH^- , and are thus basic.

Example: Consider the weak acid

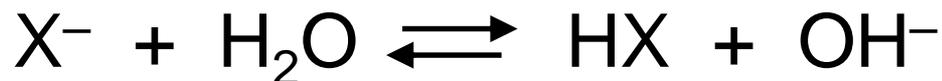


By the very definition of a weak acid, X^- does NOT like to walk alone down the Boulevard of Broken Dreams.



Now, say we have $\text{X}^-(\text{aq})$ in solution from a salt.

We'll get...



i.e., X^- accepts protons, acting like a base

Anions of strong acids do NOT influence pH.

e.g., NO_3^- (from, say, KNO_3) wants NOTHING to do with H^+ .

Anions that still have ionizable protons (e.g., HSO_3^-) are amphoteric.

-- For such substances, the larger of K_a or K_b determines the pH.



For
“amphoterics...”

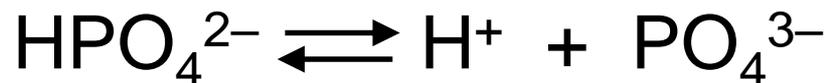
K_a
 K_b } ACID

K_a
 K_b } BASE

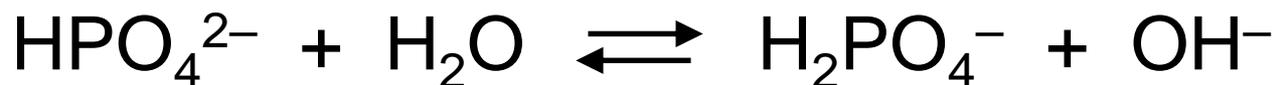
Does Na_2HPO_4 form an acidic or a basic solution in water?

Real question is: “How does HPO_4^{2-} behave?”

Like an acid...



...or a base?



From a reference table, we find...





Compare (c) going forward with (b) going in reverse.

K_{a3}

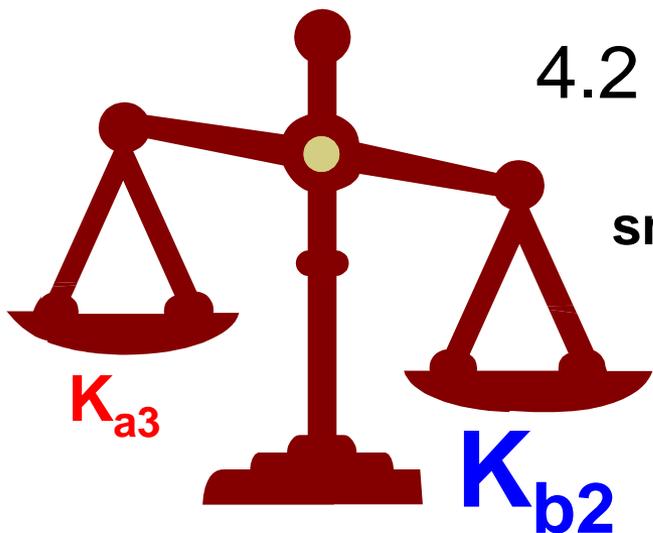
4.2×10^{-13}

smaller.

“conjugatized” K_{b2}

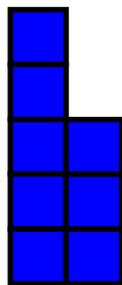
1.6×10^{-7}

BIGGER.



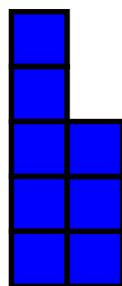
Na_2HPO_4 acts as a base.

Most cations
free-up H⁺ ions.



All cations except
act as weak acids
in aqueous solutions,
e.g.,



-- the  cations
do NOT affect pH

Predicting pH for salts derived from a...

(1) ...strong base and a strong acid

e.g., NaCl ; $\text{Ca}(\text{NO}_3)_2$

-- $\text{pH} = 7$



$\text{pH} = 7$

(2) ...strong base and a weak acid

e.g., NaClO ; $\text{Ba}(\text{CH}_3\text{COO})_2$

-- $\text{pH} > 7$



$\text{pH} > 7$

(3) ...weak base and a strong acid

e.g., NH_4Cl ; $\text{Al}(\text{NO}_3)_3$

-- $\text{pH} < 7$

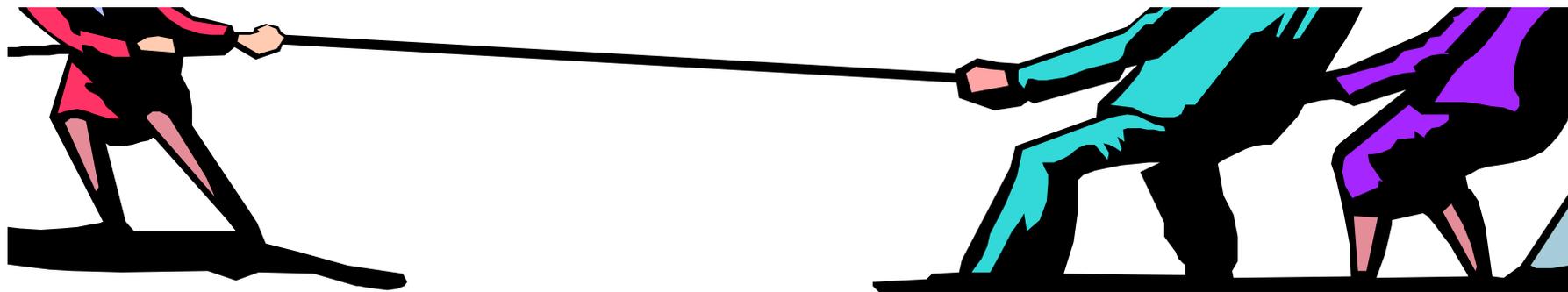
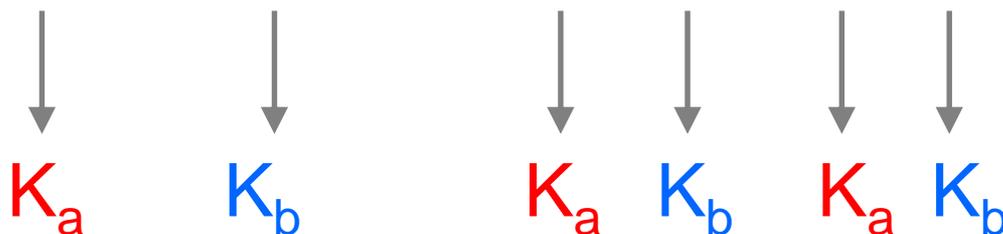


$\text{pH} < 7$

(4) ...weak base and a weak acid

- compare K_a for cation ^w/ K_b for anion;
the pH goes the way of the larger

e.g., $\text{NH}_4\text{CH}_3\text{COO}$; NH_4CN ; FeSO_3



Example: Is $\text{NH}_4\text{CN}(\text{aq})$ acidic or basic?

What related info is found in the ref. tables?

$$K_b \text{ for } \text{NH}_3 = 1.8 \times 10^{-5}$$

(for NH_3 to gain a proton)

$$K_a \text{ for } \text{HCN} = 6.2 \times 10^{-10}$$

(for HCN to lose a proton)

But we have NH_4^+ , not NH_3 , and NH_4^+ would lose a proton, so we need its K_a .

$$\text{“conjugatized” } K_a \text{ for } \text{NH}_4^+ = 5.6 \times 10^{-10}$$

And we have CN^- , not HCN , and CN^- would gain a proton, so we need its K_b .

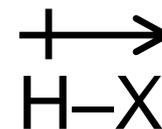
$$\text{“conjugatized” } K_b \text{ for } \text{CN}^- = 1.6 \times 10^{-5}$$

K_b is larger: $\text{NH}_4\text{CN}(\text{aq})$ is basic ($\text{pH} > 7$).

Acid-Base Behavior and Chemical Structure

Three Factors Affecting Acid Strength

1. To transfer H^+ , acid must have the polarity...



-- ionic hydrides don't (NaH, Na-H)

-- C-H bonds don't (They're nonpolar.)

As polarity increases, acid strength
generally increases. BUT...

2. ...if H-X bond is too strong... acid is weak

(e.g., HF)

3. Stable conjugate bases (e.g.,)
usually indicate a... strong acid.

For binary acids:

(1) Down a group,

bond strength is the determining factor.

...charge separation ↑, so bond strength ↓
and acid strength ↑

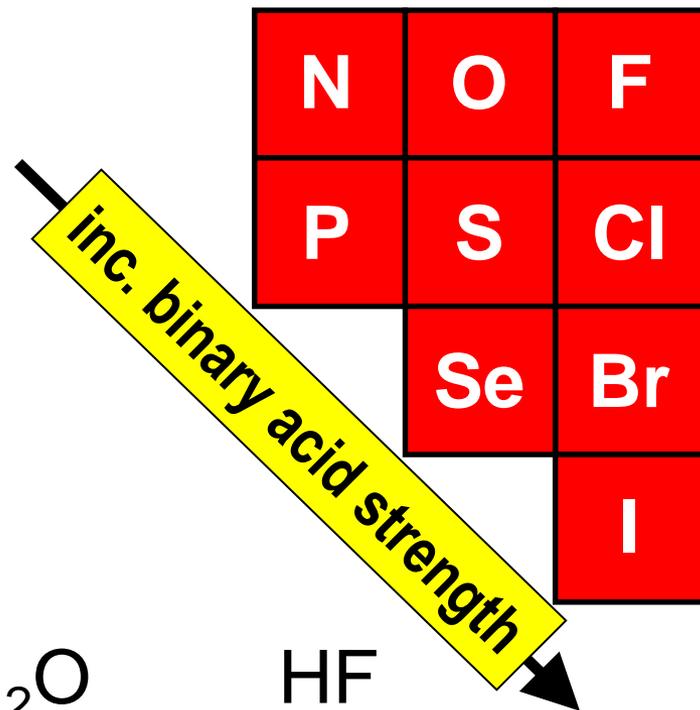
HCl HBr HI
weaker stronger

(2) Across a period,

polarity governs.

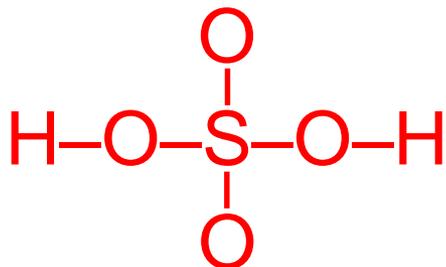
...polarity ↑ and
acid strength ↑

H₂O HF
weaker stronger



oxyacids: contain O

Consider H_2SO_4 (an acid) and $\text{Ca}(\text{OH})_2$ (a base).



The electronegativity of S is similar to that of O, so the S–O bonds are covalent. This means that... in soln, only H is released.

H_2O splits a particle where the polarity is greatest.



The electronegativity of Ca is low, while for O, it is high. Thus, the Ca–O bonds are ionic. This means that... in soln, the entire OH^- group is released.

Other tips:

(1) For oxyacids, acid strength generally increases with increasing electronegativity of the central atom.

e.g., HClO stronger

HBrO (because $EN_{Cl} > EN_{Br} > EN_I$)

HIO weaker

(2) For oxyacids with the same central atom, acid strength increases as the number of oxygens attached to the central atom increases.

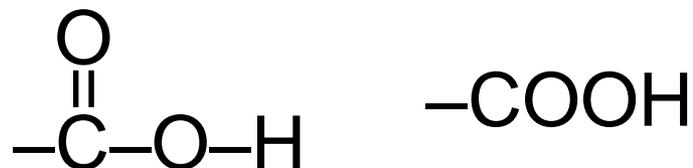
e.g., HClO weaker

HClO₂

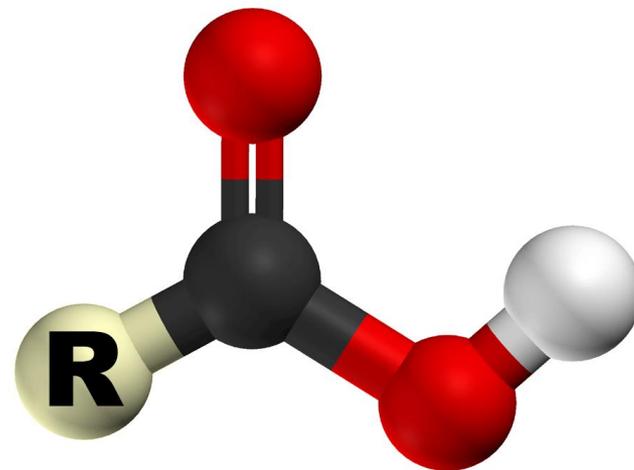
HClO₃

HClO₄ stronger

Carboxylic acids contain the carboxyl group.



- these comprise the largest category of organic acids
- acid strength increases with the addition of more electronegative atoms



e.g., CH_3COOH weaker

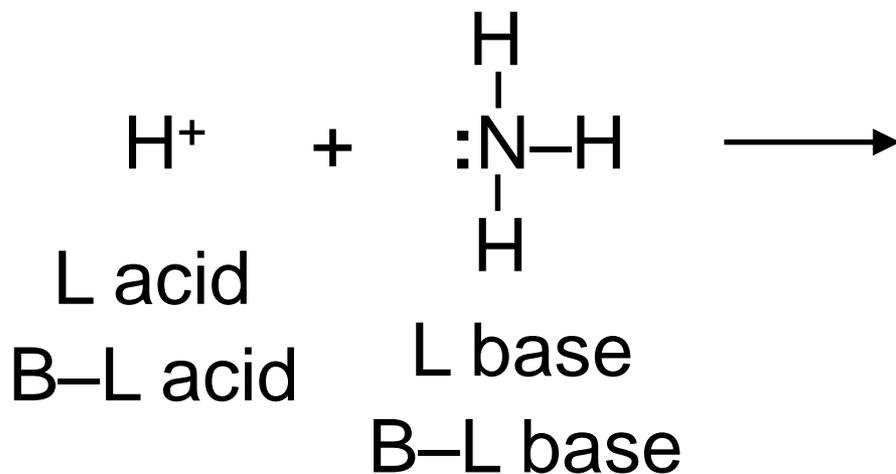
vs.

CF_3COOH stronger

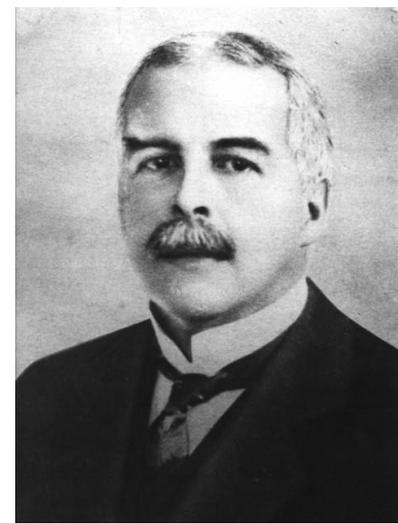
Lewis Acids and Lewis Bases

e⁻ pair acceptors

e⁻ pair donors

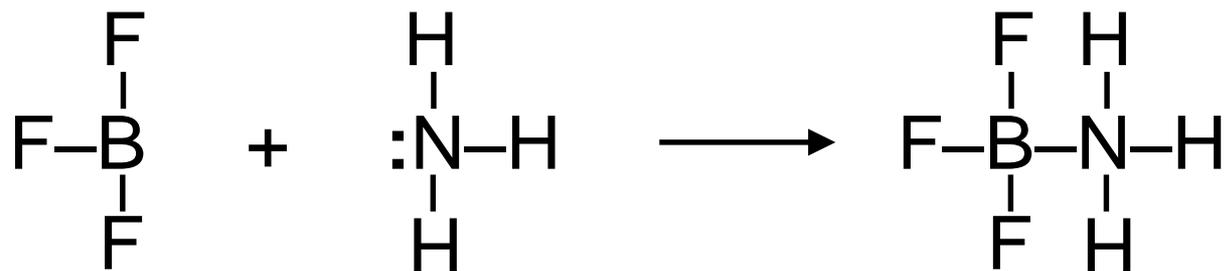


The “Lewis” definitions greatly broaden the range of acids because many species other than H-containing ones can accept an e⁻ pair.



Gilbert Lewis
(1875–1946)

Another example:



L acid

L base

The simple term “acid” suggests that we are referring to an Arrhenius or a Bronsted-Lowry acid, i.e., an H-containing substance in an aqueous solution. If you are referring to a Lewis acid, then use the term “Lewis acid.”

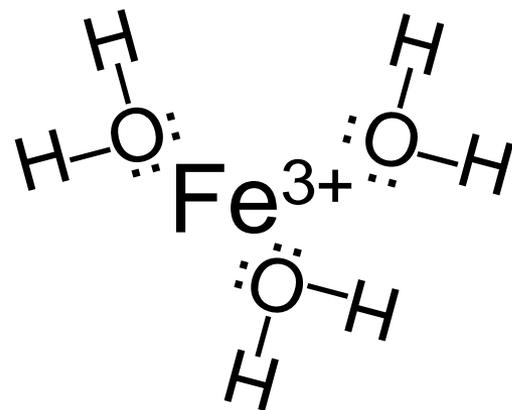


Substances with an incomplete octet (e.g., BF_3) or ones having vacant orbitals (e.g., Fe^{3+}) can function as Lewis acids.

-- this is why solns of many metal ions exhibit acidic properties

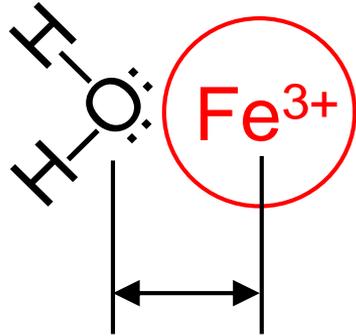
-- The (+) charge attracts (i.e., accepts) the lone pairs of e^- on the O of a water molecule. This process is hydration: the “glomming” of H_2O m'cules onto metal ions.

Solutions w/the Fe^{3+} ion exhibit a characteristic orange color and are generally acidic.



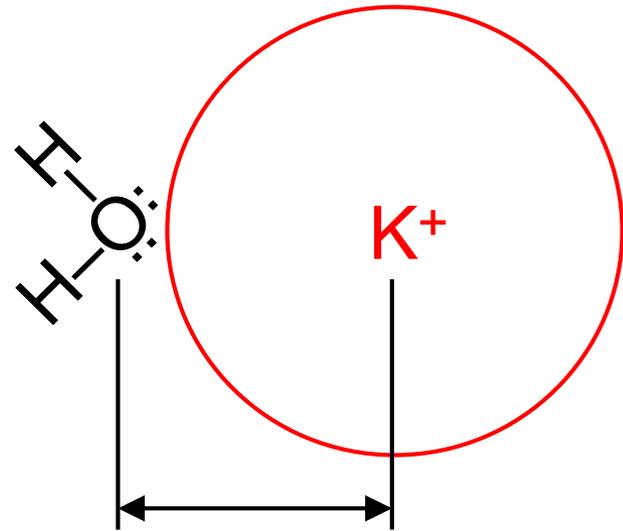
e^- pair acceptor
(L acid)

Cation size and cation charge determine the extent to which the pH is affected.



- short distance
- strong interaction
- O–H becomes more polarized, and “more polarized” = “stronger acid”

(i.e., H⁺s more likely to pop off)



- larger distance
- weaker interaction
- O–H bond keeps ~ same polarity; acidity is unaffected