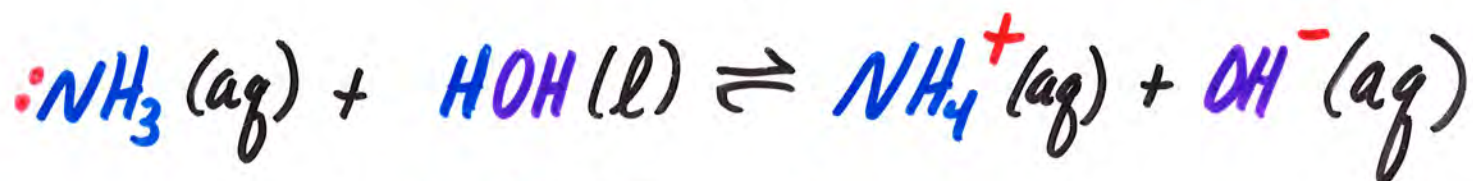


IV) Weak Bases

A Base accepts a H^+ from H_2O producing OH^-

- rx. does **not** go to completion



$$K = \frac{[NH_4^+][OH^-]}{[NH_3][HOH]}$$

$$K[HOH] = K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Base-Ionization Constant

weaker base \Rightarrow smaller K_b

A) Amines



substituted ammonia

Lone-pair e^- that accept H^+



$$K_b = 4.4 \times 10^{-4}$$

Substance	Formula	K_b
Ammonia	NH_3	1.8×10^{-5}
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	4.2×10^{-10}
Dimethylamine	$(\text{CH}_3)_2\text{NH}$	5.1×10^{-4}
Ethylamine	$\text{C}_2\text{H}_5\text{NH}_2$	4.7×10^{-4}
Hydrazine	N_2H_4	1.7×10^{-6}
Hydroxylamine	NH_2OH	1.1×10^{-8}
Methylamine	CH_3NH_2	4.4×10^{-4}
Pyridine	$\text{C}_5\text{H}_5\text{N}$	1.4×10^{-9}
Urea	NH_2CONH_2	1.5×10^{-14}

1) Ex 1: The pH of a 0.100 M CH_3NH_2 soln. is 11.81.
What is K_b ?



$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\ddot{\text{N}}\text{H}_2]}$$

$$p\text{OH} =$$

$$[\text{OH}^-] =$$

$$[\text{CH}_3\text{NH}_3^+] =$$

$$[\text{CH}_3\ddot{\text{N}}\text{H}_2] =$$

$$K_b =$$

B) Anions of Weak Acids



$$K_a = 1.8 \times 10^{-5}$$

$\text{C}_2\text{H}_3\text{O}_2^-$ is conjugate base
of a weak acid



$$K_b = 5.6 \times 10^{-10}$$

VII) Acid/Base Strength & K_a , pK_a , K_b , pK_b

$$pK_a = -\log K_a \quad pK_b = -\log K_b$$

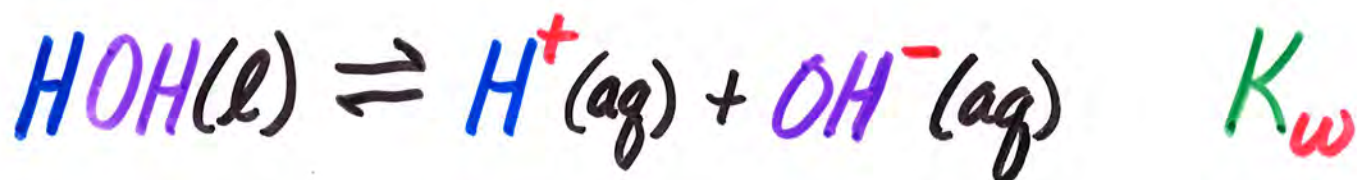
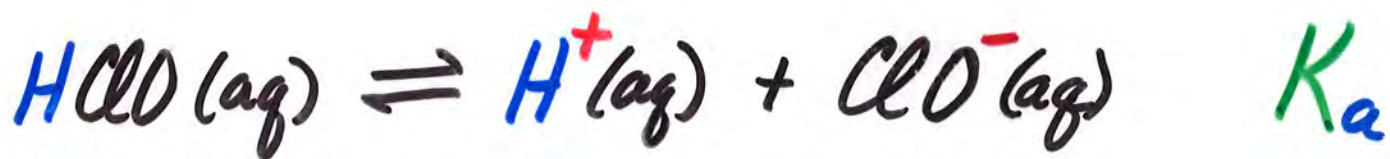
$$K_a = 1.0 \times 10^{-1}, \quad pK_a = 1$$

$$K_a = 1.0 \times 10^{-10}, \quad pK_a = 10$$

Stronger Acid \Rightarrow Larger K_a \Rightarrow Smaller pK_a

Stronger Base \Rightarrow Larger K_b \Rightarrow Smaller pK_b

VIII) Relationship between K_a & K_b



$$K_w = [\text{H}^+][\text{OH}^-]$$

General Rule

If 2 rx's (eqn's) can be added to give a 3rd rx. (eqn.) then

K_3 is product of K_1 & K_2



$$K_1 \times K_2 = K_3$$

$$K_a \cdot K_b = \left(\frac{[H^+][ClO^-]}{[HClO]} \right) \cdot \left(\frac{[HClO][OH^-]}{[ClO^-]} \right)$$

$$= [H^+][OH^-]$$

$$K_a \cdot K_b = K_w$$

Note: For conjugate acid-base pair

$$K_{\text{acid}} \times K_{\text{conj. base}} = K_w$$

stronger
acid



weaker
conj. base

(larger K_a)

(smaller K_b)

At 25°C

$$K_a \times K_b = 1.0 \times 10^{-14}$$

$$pK_a + pK_b = pK_w = 14.00$$

1) Ex 1: What is the K_a
for HClO given $K_b = 3.3 \times 10^{-7}$
for ClO^- ? Also, what
are the pK_a & pK_b ?

IX) Hydrolysis: Salt Solutions

Rxn. of an ion w.
 H_2O to produce



Cations: produce H_3O^+

Anions: produce OH^-

II) Anion Hydrolysis

Conjugate bases of weak acids

- relatively strong bases



Anions of strong acids do
NOT hydrolyze

- do **NOT** act as bases



Ex: Calc. pH of 0.20 M NaF

NaF in H₂O - strong electrolyte



does NOT hydrolyze
(Grp. IA & IIA)

weak base
- hydrolyzes to produce OH⁻

	$F^- + H_2O \rightleftharpoons HF + OH^-$		
init.	0.20	0	0
chg.	-x	+x	+x
equil.	0.20-x	x	x

$$K_b = \frac{[HF][OH^-]}{[F^-]} = ?$$

K_b for F⁻ & other anions of weak acids not listed in tables

Calc. K_b from K_a for the
conjugate acid.

$$K_{b_{F^-}} = \frac{[HF][OH^-]}{[F^-]} =$$

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{x^2}{(0.20-x)} = \frac{x^2}{0.20} = 1.5 \times 10^{-11}$$

$$x = [OH^-] = [HF] = 1.7 \times 10^{-6}$$

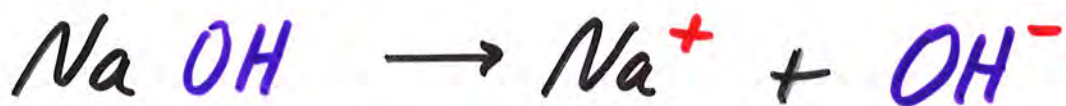
$$pOH = 5.76$$

$$pH = 8.24$$

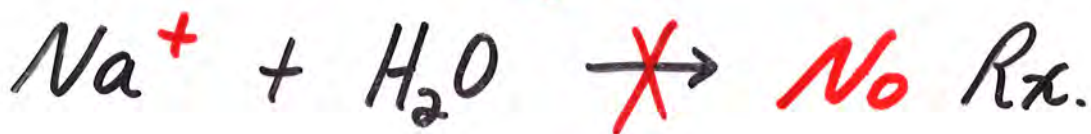
B) Cation Hydrolysis

1) Group IA + IIA Cations

Do **NOT** hydrolyze



- **completely** dissociates



2) Hydrated Metal Cations



Transition Metals &

non-Group IA + IIA Metals

form **weakly acidic** soln.'s

3) Conjugate Acid of Weak Base



Ex: Calc. pH of 0.20 M $\text{CH}_3\text{NH}_3\text{Cl}$.

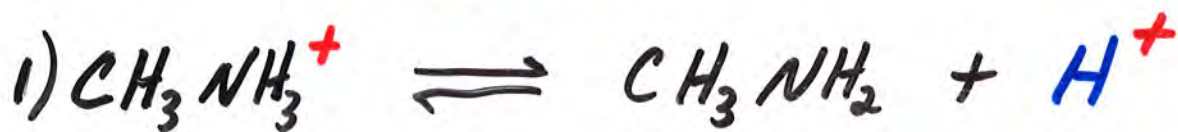
K_b of CH_3NH_2 is 4.4×10^{-4}

$$K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}^+]}{[\text{CH}_3\text{NH}_3^+]} = \frac{K_w}{K_b} = 2.3 \times 10^{-11}$$

c) Both Cation & Anion Hydrolysis

Salt of weak acid & weak base

pH depends on extent to which each ion hydrolyzes.



$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.3 \times 10^{-11}$$



$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

$K_a > K_b \Rightarrow$ Rx (1) goes little farther toward completion

$[\text{H}^+] > [\text{OH}^-] \Rightarrow$ Soln. slightly acidic

D) Soln. of Acidic Salt



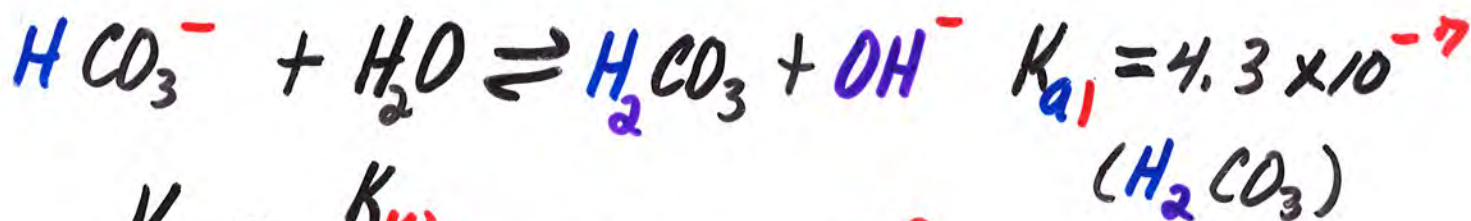
HCO_3^- : Amphoteric

Look at both acid ionization
& anion hydrolysis.

1) Acid Ionization



2) Anion Hydrolysis



$$K_b = \frac{K_w}{K_{a1}} = 2.3 \times 10^{-8}$$

$K_b > K_{a2} \Rightarrow$ soln. is Basic

E) Summary

1) Salt of strong acid & strong base



$$\text{pH} = 7$$

2) Salt of weak acid & strong base



$$\text{pH} > 7$$

3) Salt of strong acid & weak base



$$\text{pH} < 7$$

4) Salt of weak acid & weak base



pH depends on sizes of K_a
of acid & K_b of base

IV) Molecular Structure & Acid Strength

A) Binary Acids : HX

HX bond must be polar



- More polar bond \Rightarrow stronger acid
- bond strength is important
 - strong bonds not easily ionized
- More stable conj. base \Rightarrow stronger acid

Ex: Hydrogen Halides ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$)



HF is a weak acid

- most polar bond
- but, strongest bond

1) Down a Column in P.T.

- size of X inc.
- HX bond strength dec.
- stability of resulting anion inc.
- strength of binary acid inc.



2) Across a Period in P.T.

- radius of X dec. slowly
- polarity of bond most imp.
- electroneg. of X inc. \longrightarrow
- bond polarity inc.
- strength of acid inc.

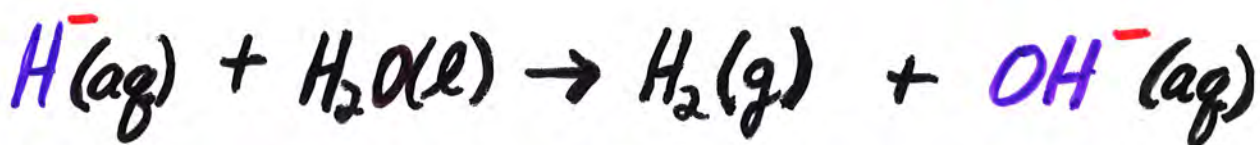
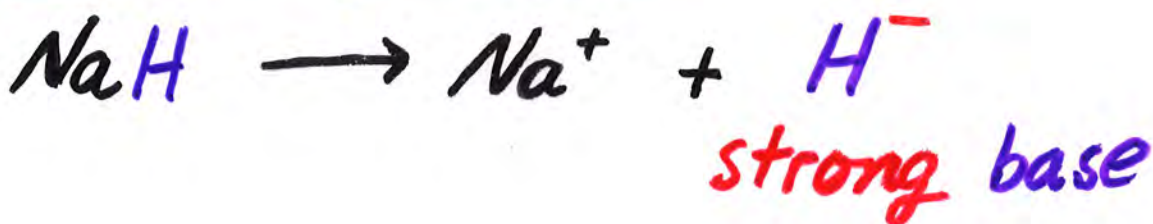


3) Non polar Substances

Do **NOT** hydrolyze

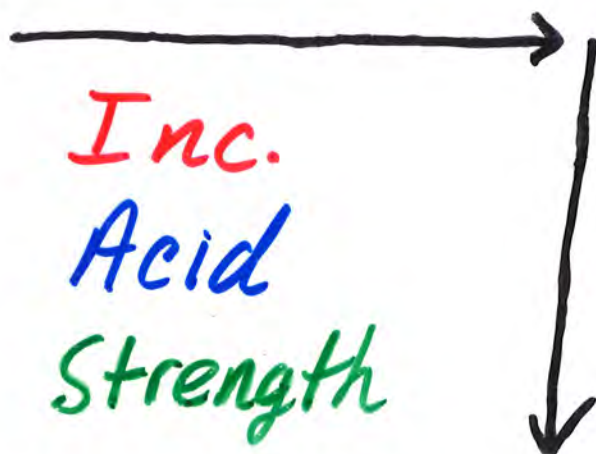
Neutral

4) Metal Hydrides



Basic Hydrides

5) Summary (Binary Acids)



B) Ternary Acids (Oxyacids)



H-O bond polarity most imp't.

1) Type 1

Same structure, diff. central atom Y

- acid strength inc. w. E.N. of Y



H-O bond polarity inc.

- easier for H^+ to leave



2) Type 2



same central atom Y,

diff. number of nonprotonated

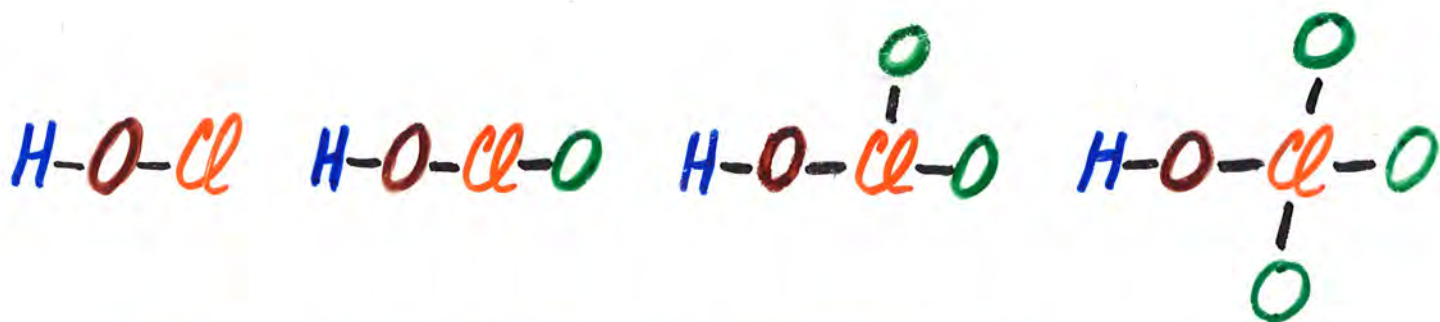
O-atoms bonded to Y

Acidity inc. w.:

inc. # O-atoms

+

inc. ox. # of Y



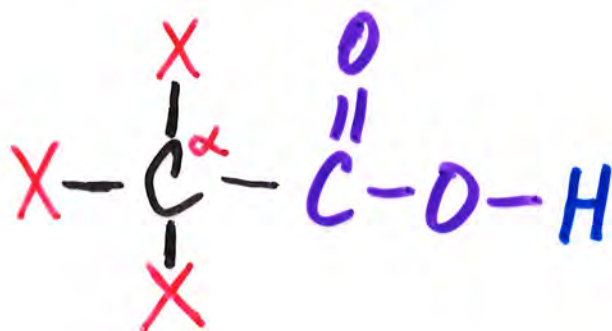
+1

+3

+5

+7

c) Carboxylic Acids



X = H, C-group;
or

Electron Withdrawing Group
(Halogens, O, N)

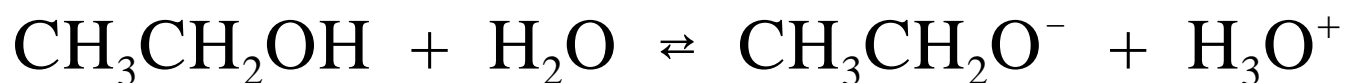
Acid Strength:

Inc. w. inc. EN of α -substituent

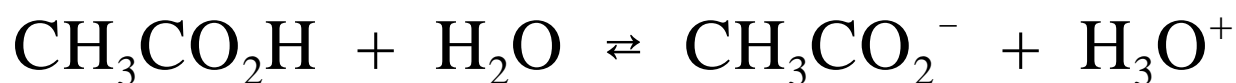


Inc. w. number of EWG

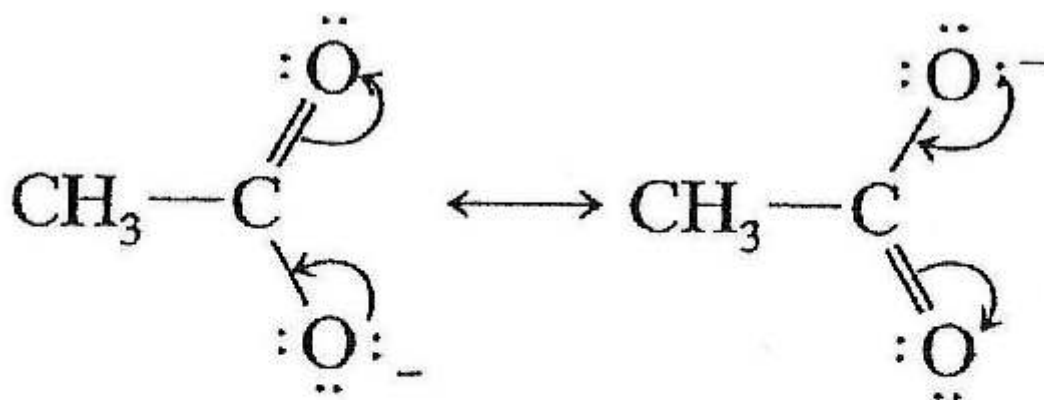




$$K_a = 1 \times 10^{-16}$$



$$K_a = 1.8 \times 10^{-5}$$

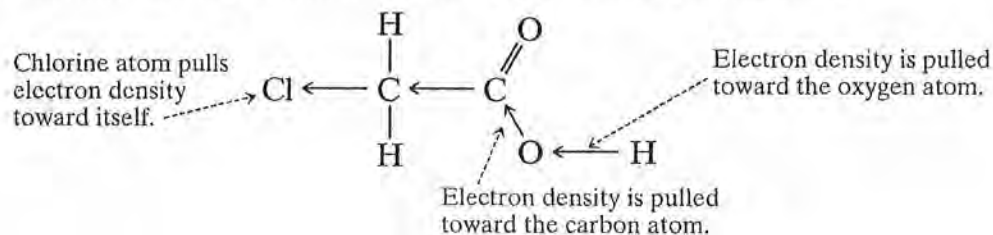


resonance contributors of acetate ion

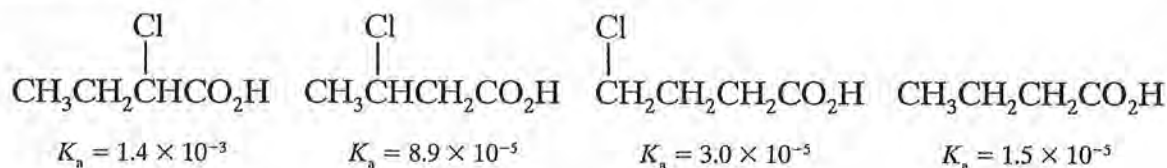
TABLE 18.3 Effect of Substituents on Acidity of Carboxylic Acids

Name of Acid	Formula	K_a	pK_a
acetic acid	$\text{CH}_3\text{CO}_2\text{H}$	1.8×10^{-5}	4.7
butyric acid	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$	1.3×10^{-5}	4.9
isobutyric acid	$(\text{CH}_3)_2\text{CHCO}_2\text{H}$	1.6×10^{-5}	4.8
fluoroacetic acid	$\text{FCH}_2\text{CO}_2\text{H}$	2.5×10^{-3}	2.6
chloroacetic acid	$\text{ClCH}_2\text{CO}_2\text{H}$	1.4×10^{-3}	2.9
dichloroacetic acid	$\text{Cl}_2\text{CHCO}_2\text{H}$	5.0×10^{-2}	1.3
trichloroacetic acid	$\text{Cl}_3\text{CCO}_2\text{H}$	2.5×10^{-1}	0.6

ther increases its acidity. For example, halogen atoms pull electron density away from the carbon skeleton, and indirectly from the O—H bond. As a consequence, the proton is more easily removed and K_a increases (Table 18.3).



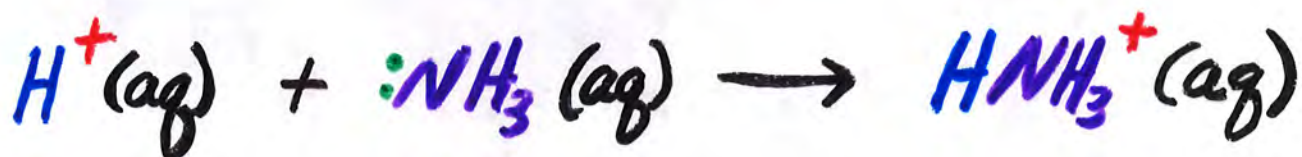
As the distance between the halogen atom and the carboxyl group increases, the inductive effect falls off dramatically. For β - and γ -substituted acids, the K_a values approach that of an unsubstituted carboxylic acid.



IX) Lewis Acid-Base Theory

Lewis Acid: e^- -pair acceptor

Lewis Base: e^- -pair donor



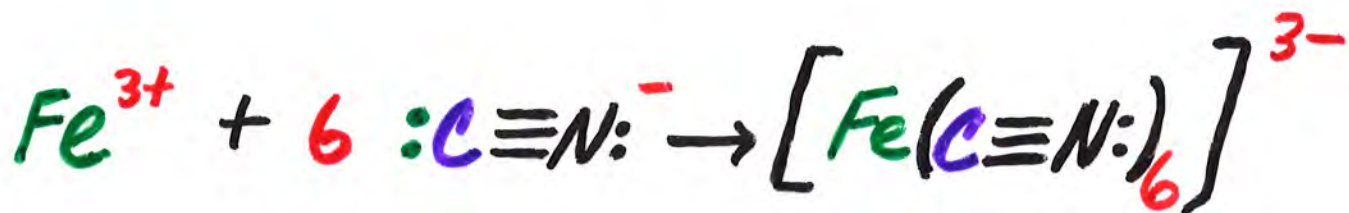
Acid
(acceptor) Base
(donor)

BF_3 : B is e^- -deficient
(empty p-orbital
- incomplete octet)

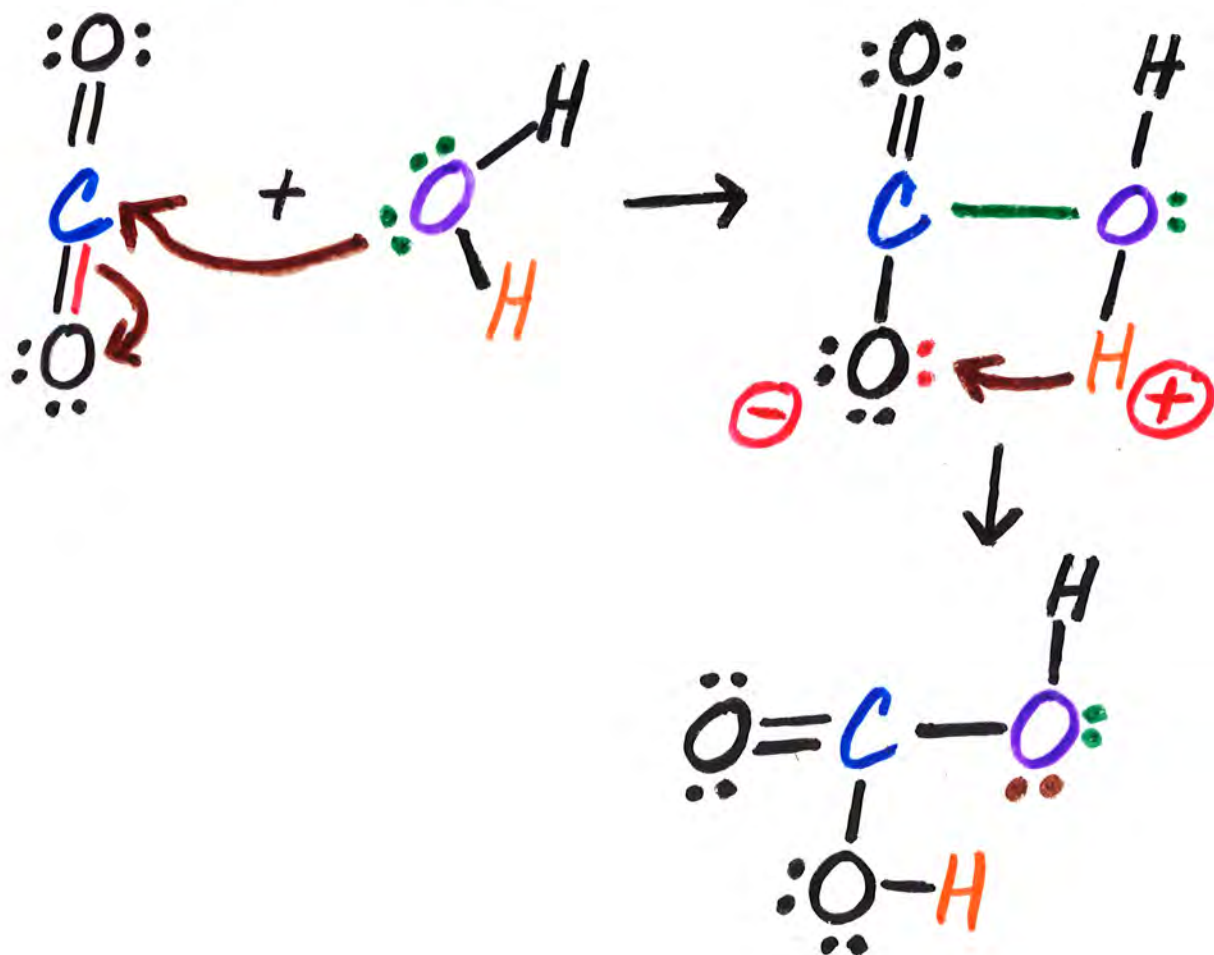


A) Metal Cations

Fe^{3+} : empty d-orbitals

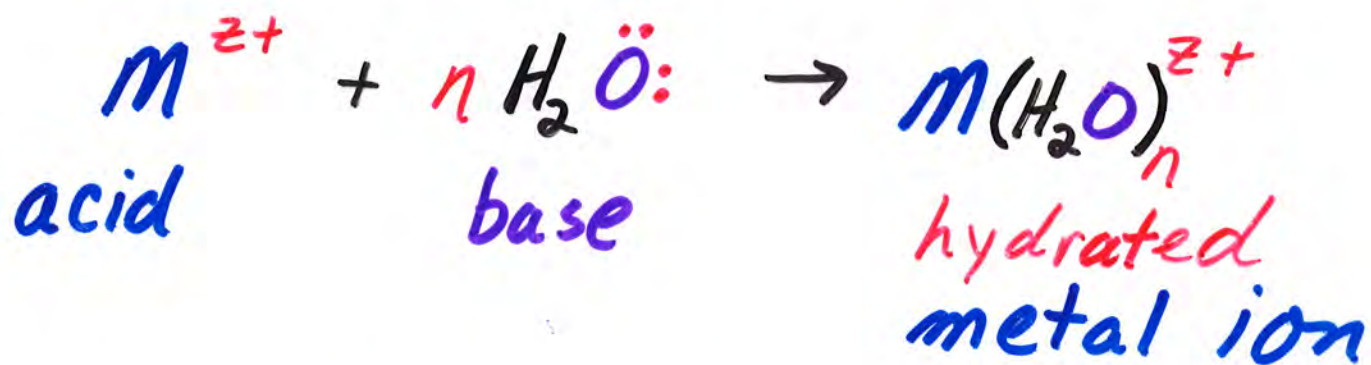


B) Nonmetal Compds w. Multiple Bonds



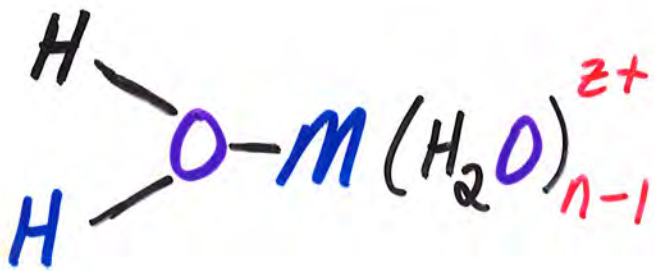
c) Hydrolysis of Metal Ions

Metal Ions in $H_2\ddot{O}$ are
Hydrated

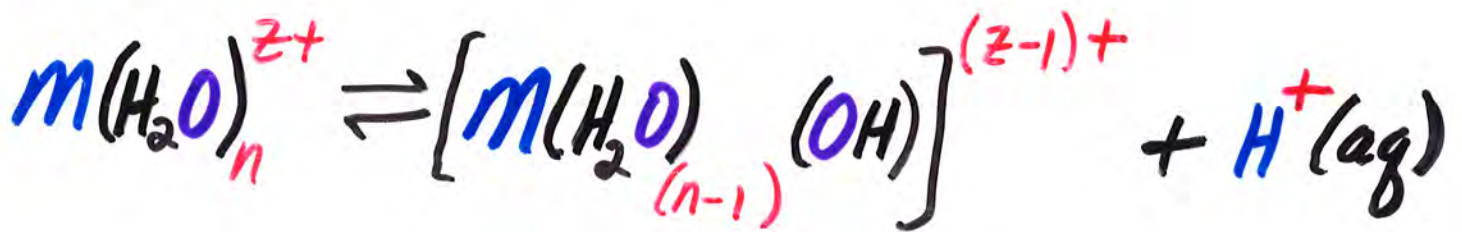


strength of attraction inc. w.
ion charge + as size of
ion dec.

- Look at ratio: $\frac{\text{charge}}{\text{radius}}$



M^{z+} draws e^- -density away from O-H
 \Rightarrow O-H bond more polarized
 - more acidic



$K_a \equiv$ Acid Hydrolysis Constant

K_a inc. as $\frac{\text{chg.}}{\text{rad.}}$ inc.

Ex : Given K_a values of 6.8×10^{-8} & 1.0×10^{-10} for $C_5H_5NH^+$ & C_6H_5OH respectively, calc. the equilibrium constant for the following reaction.



