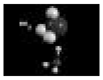
Acids and Bases: A Brief Review

- Acids: taste sour and cause dyes to change color.
- Bases: taste bitter and feel soapy.
- Arrhenius: acids increase $[H^+]$ bases increase $[OH^-]$ in solution.
- Arrhenius: acid + base → salt + water.
- Problem: the definition confines us to aqueous solution.



Brønsted-Lowry Acids and Bases

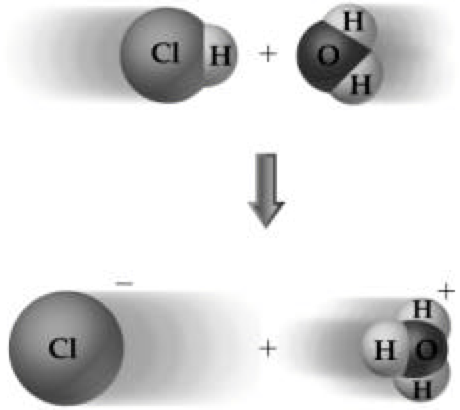
The H^+ Ion in Water

- The $H^+(aq)$ ion is simply a proton with no electrons. (H has one proton, one electron, and no neutrons.)
- In water, the $H^+(aq)$ form clusters.
- The simplest cluster is $H_3O^+(aq)$. Larger clusters are $H_5O_2^+$ and $H_9O_4^+$.
- Generally we use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably.

Brønsted-Lowry Acids and Bases

Proton Transfer Reactions

- Focus on the $H^+(aq)$.
- Brønsted-Lowry: acid donates H^+ and base accepts H^+.
- Brønsted-Lowry base does not need to contain OH^-.
- Consider $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$:
  - HCl donates a proton to water. Therefore, HCl is an acid.
  - H_2O accepts a proton from HCl. Therefore, H_2O is a base.
- Water can behave as either an acid or a base.
- Amphoteric substances can behave as acids and bases.



Brønsted-Lowry Acids and Bases

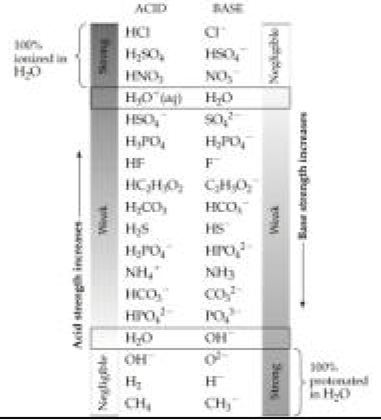
Conjugate Acid-Base Pairs

- Whatever is left of the acid after the proton is donated is called its conjugate base.
- Similarly, whatever remains of the base after it accepts a proton is called a conjugate acid.
- Consider $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$
  - After HA (acid) loses its proton it is converted into A^- (base). Therefore HA and A^- are conjugate acid-base pairs.
  - After H_2O (base) gains a proton it is converted into H_3O^+ (acid). Therefore, H_2O and H_3O^+ are conjugate acid-base pairs.
- Conjugate acid-base pairs differ by only one proton.

Brønsted-Lowry Acids and Bases

Relative Strengths of Acids and Bases

- The stronger the acid, the weaker the conjugate base.
- H^+ is the strongest acid that can exist in equilibrium in aqueous solution.
- OH^- is the strongest base that can exist in equilibrium in aqueous solution.



ACID	BASE
HCl	Cl^-
H_2SO_4	HSO_4^-
HNO_3	NO_3^-
$H_3O^+(aq)$	H_2O
HSO_4^-	SO_4^{2-}
H_3PO_4	$H_2PO_4^-$
HF	F^-
$HC_2H_3O_2$	$C_2H_3O_2^-$
H_2CO_3	HCO_3^-
H_2S	HS^-
$H_2PO_4^-$	HPO_4^{2-}
NH_4^+	NH_3
HCO_3^-	CO_3^{2-}
HPO_4^{2-}	PO_4^{3-}
H_2O	OH^-
OH^-	O^{2-}
H_2	H^-
CH_4	CH_3^-

Brønsted-Lowry Acids and Bases

Relative Strengths of Acids and Bases

- Any acid or base that is stronger than H^+ or OH^- simply reacts stoichiometrically to produce H^+ and OH^-.
- The conjugate base of a strong acid (e.g. Cl^-) has negligible acid-base properties.
- Similarly, the conjugate acid of a strong base has negligible acid-base properties.

The Autoionization of Water

The Ion Product of Water

- In pure water the following equilibrium is established

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

- at 25 °C

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$K_{eq} \times [H_2O]^2 = [H_3O^+][OH^-]$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

- The above is called the autoionization of water.

The pH Scale

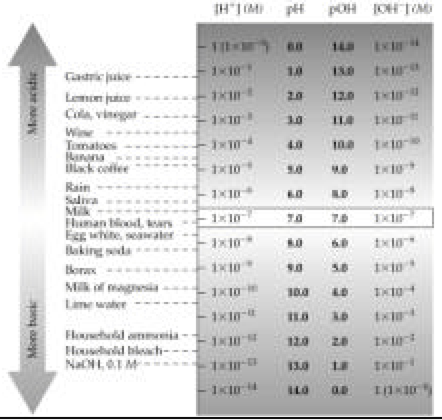
- In most solutions $[H^+(aq)]$ is quite small.
- We define

$$pH = -\log[H_3O^+] = -\log[H^+] \qquad pOH = -\log[OH^-]$$

- In neutral water at 25 °C, pH = pOH = 7.00.
- In acidic solutions, $[H^+] > 1.0 \times 10^{-7}$, so pH < 7.00.
- In basic solutions, $[H^+] < 1.0 \times 10^{-7}$, so pH > 7.00.
- The higher the pH, the lower the pOH, the more basic the solution.

The pH Scale

- Most pH and pOH values fall between 0 and 14.
- There are no theoretical limits on the values of pH or pOH. (e.g. pH of 2.0 *M* HCl is -0.301.)



$[H^+]$ (*M*)	pH	pOH	$[OH^-]$ (*M*)
$1\ (1\times10^{-0})$	0.0	14.0	1×10^{-14}
1×10^{-1}	1.0	13.0	1×10^{-13}
1×10^{-2}	2.0	12.0	1×10^{-12}
1×10^{-3}	3.0	11.0	1×10^{-11}
1×10^{-4}	4.0	10.0	1×10^{-10}
1×10^{-5}	5.0	9.0	1×10^{-9}
1×10^{-6}	6.0	8.0	1×10^{-8}
1×10^{-7}	7.0	7.0	1×10^{-7}
1×10^{-8}	8.0	6.0	1×10^{-6}
1×10^{-9}	9.0	5.0	1×10^{-5}
1×10^{-10}	10.0	4.0	1×10^{-4}
1×10^{-11}	11.0	3.0	1×10^{-3}
1×10^{-12}	12.0	2.0	1×10^{-2}
1×10^{-13}	13.0	1.0	1×10^{-1}
1×10^{-14}	14.0	0.0	$1\ (1\times10^{-0})$

The pH Scale

Other "p" Scales

- In general for a number X,

$$\mathrm{pX} = -\log X$$

- For example, pK_w = -log K_w.

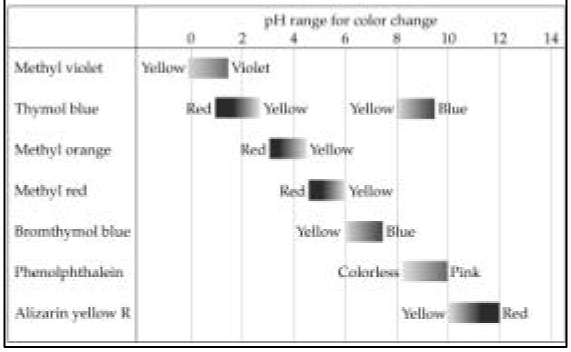
$$K_w = [\mathrm{H}^+][\mathrm{OH}^-] = 1.0\times10^{-14}$$
$$\mathrm{pK}_w = -\log\left([\mathrm{H}^+][\mathrm{OH}^-]\right) = 14$$
$$\therefore -\log[\mathrm{H}^+] - \log[\mathrm{OH}^-] = 14$$
$$\mathrm{pH} + \mathrm{pOH} = 14$$

The pH Scale

Measuring pH

- Most accurate method to measure pH is to use a pH meter.
- However, certain dyes change color as pH changes. These are indicators.
- Indicators are less precise than pH meters.
- Many indicators do not have a sharp color change as a function of pH.
- Most indicators tend to be red in more acidic solutions.

The pH Scale



Strong Acids and Bases

Strong Acids

- The strongest common acids are HCl, HBr, HI, HNO_3, $HClO_3$, $HClO_4$, and H_2SO_4.
- Strong acids are strong electrolytes.
- All strong acids ionize completely in solution:

$$\mathrm{HNO_3}(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{H_3O^+}(aq) + \mathrm{NO_3^-}(aq)$$

- Since H^+ and H_3O^+ are used interchangeably, we write

$$\mathrm{HNO_3}(aq) \rightarrow \mathrm{H^+}(aq) + \mathrm{NO_3^-}(aq)$$

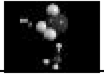
Strong Acids and Bases

Strong Acids

- In solutions the strong acid is usually the only source of H^+. (If the molarity of the acid is less than 10^{-6} *M* then the autoionization of water needs to be taken into account.)
- Therefore, the pH of the solution is the initial molarity of the acid.

Strong Bases

- Most ionic hydroxides are strong bases (e.g. NaOH, KOH, and $Ca(OH)_2$).



Strong Acids and Bases

Strong Bases

- Strong bases are strong electrolytes and dissociate completely in solution.
- The pOH (and hence pH) of a strong base is given by the initial molarity of the base. *Be careful of stoichiometry*.
- In order for a hydroxide to be a base, it must be soluble.
- Bases do not have to contain the OH^- ion:

$$\mathrm{O^{2-}}(aq) + \mathrm{H_2O}(l) \rightarrow 2\mathrm{OH^-}(aq)$$
$$\mathrm{H^-}(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{H_2}(g) + \mathrm{OH^-}(aq)$$
$$\mathrm{N_3^-}(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{NH_3}(aq) + 3\mathrm{OH^-}(aq)$$

Weak Acids

- Weak acids are only partially ionized in solution.
- There is a mixture of ions and unionized acid in solution.
- Therefore, weak acids are in equilibrium:

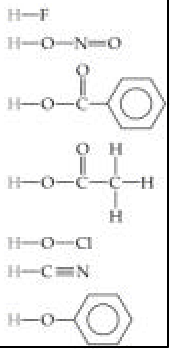
$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

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

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

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

Weak Acids



- K_a is the acid dissociation constant.
- Note $[H_2O]$ is omitted from the K_a expression. (H_2O is a pure liquid.)
- The larger the K_a the stronger the acid (i.e. the more ions are present at equilibrium relative to unionized molecules).
- If $K_a >> 1$, then the acid is completely ionized and the acid is a strong acid.

Weak Acids

Calculating K_a from pH

- Weak acids are simply equilibrium calculations.
- The pH gives the equilibrium concentration of H^+.
- Using K_a, the concentration of H^+ (and hence the pH) can be calculated.
  - Write the balanced chemical equation clearly showing the equilibrium.
  - Write the equilibrium expression. Find the value for K_a.
  - Write down the initial and equilibrium concentrations for everything except pure water. We usually assume that the change in concentration of H^+ is x.

Weak Acids

Calculating K_a from pH

- Substitute into the equilibrium constant expression and solve. Remember to turn x into pH if necessary.

Using K_a to Calculate pH

- Percent ionization is another method to assess acid strength.
- For the reaction

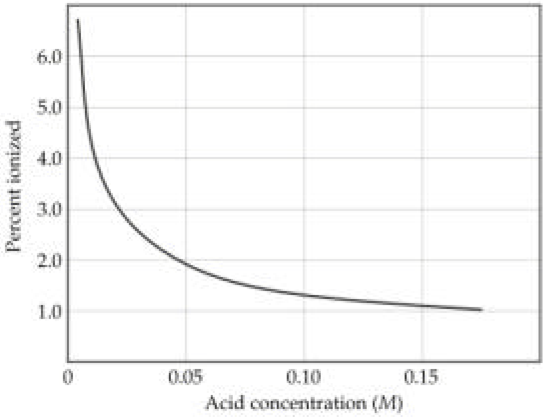
$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$\%\,\text{ionization} = \frac{[H_3O^+]_{eqm}}{[HA]_0} \times 100$$

Weak Acids

Using K_a to Calculate pH

- Percent ionization relates the equilibrium H^+ concentration, $[H^+]_{eqm}$, to the initial HA concentration, $[HA]_0$.
- The higher percent ionization, the stronger the acid.
- Percent ionization of a weak acid decreases as the molarity of the solution increases.
- For acetic acid, 0.05 M solution is 2.0 % ionized whereas a 0.15 M solution is 1.0 % ionized.



Weak Acids

Polyprotic Acids

- Polyprotic acids have more than one ionizable proton.
- The protons are removed in steps not all at once:

$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \quad K_{a1} = 1.7 \text{ x } 10^{-2}$$

$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \quad K_{a2} = 6.4 \text{ x } 10^{-8}$$

- It is always easier to remove the first proton in a polyprotic acid than the second.
- Therefore, $K_{a1} > K_{a2} > K_{a3}$ etc.

Weak Acids

Polyprotic Acids

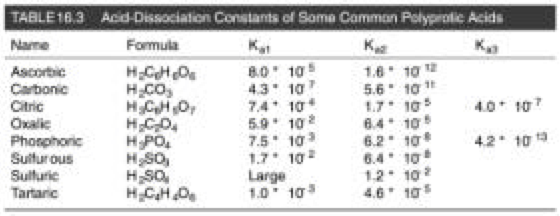


TABLE 16.3 Acid-Dissociation Constants of Some Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Ascorbic	$H_2C_6H_6O_6$	8.0 * 10^{5}	1.6 * 10^{12}	
Carbonic	H_2CO_3	4.3 * 10^{7}	5.6 * 10^{11}	
Citric	$H_3C_6H_5O_7$	7.4 * 10^{4}	1.7 * 10^{5}	4.0 * 10^{7}
Oxalic	$H_2C_2O_4$	5.9 * 10^{2}	6.4 * 10^{5}	
Phosphoric	H_3PO_4	7.5 * 10^{3}	6.2 * 10^{8}	4.2 * 10^{13}
Sulfurous	H_2SO_3	1.7 * 10^{2}	6.4 * 10^{8}	
Sulfuric	H_2SO_4	Large	1.2 * 10^{2}	
Tartaric	$H_2C_4H_4O_6$	1.0 * 10^{3}	4.6 * 10^{5}	

Weak Bases

- Weak bases remove protons from substances.
- There is an equilibrium between the base and the resulting ions:

$$\text{Weak base} + H_2O \rightleftharpoons \text{conjugate acid} + OH^-$$

- Example:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

- The base dissociation constant, K_b, is defined as

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

Weak Bases

Types of Weak Bases

- Bases generally have lone pairs or negative charges in order to attack protons.
- Most neutral weak bases contain nitrogen.
- Amines are related to ammonia and have one or more N-H bonds replaced with N-C bonds (e.g., CH_3NH_2 is methylamine).
- Anions of weak acids are also weak bases. Example: OCl^- is the conjugate base of HOCl (weak acid):

$$ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq) \quad K_b = 3.3 \text{ x } 10^{-7}$$

Relationship Between K_a and K_b

- We need to quantify the relationship between strength of acid and conjugate base.
- When two reactions are added to give a third, the equilibrium constant for the third reaction is the product of the equilibrium constants for the first two:

Reaction 1 + reaction 2 = reaction 3

has

$$K_3 = K_1 \times K_2$$

Relationship Between K_a and K_b

- For a conjugate acid-base pair

$$K_w = K_a \times K_b$$

- Therefore, the larger the K_a, the smaller the K_b. That is, the stronger the acid, the weaker the conjugate base.
- Taking negative logarithms:

$$pK_w = pK_a + pK_b$$

Relationship Between K_a and K_b

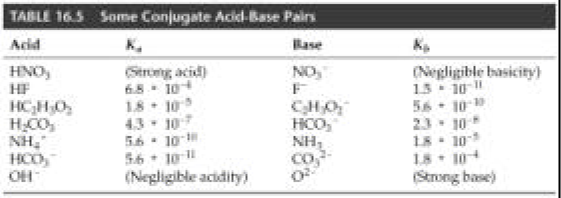


TABLE 16.5 Some Conjugate Acid-Base Pairs

Acid	K_a	Base	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^-$	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}
OH^-	(Negligible acidity)	O^{2-}	(Strong base)

Acid-Base Properties of Salt Solutions

- Nearly all salts are strong electrolytes.
- Therefore, salts exist entirely of ions in solution.
- Acid-base properties of salts are a consequence of the reaction of their *ions* in solution.
- The reaction in which ions produce H^+ or OH^- in water is called hydrolysis.
- Anions from weak acids are basic.
- Anions from strong acids are neutral.

Acid-Base Properties of Salt Solutions

An Anion's Ability to React with Water

- Anions, X^-, can be considered conjugate bases from acids, HX.
- For X^- comes from a strong acid, then it is neutral.
- If X^- comes from a weak acid, then

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

- The pH of the solution can be calculated using equilibrium!

Acid-Base Properties of Salt Solutions

An Cation's Ability to React with Water

- Polyatomic cations with ionizable protons can be considered conjugate acids of weak bases.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

- Some metal ions react in solution to lower pH.

Combined Effect of Cation and Anion in Solution

- An anion from a strong acid has no acid-base properties.
- An anion that is the conjugate base of a weak acid will cause an increase in pH.

Acid-Base Properties of Salt Solutions

Combined Effect of Cation and Anion in Solution

- A cation that is the conjugate acid of a weak base will cause a decrease in the pH of the solution.
- Metal ions will cause a decrease in pH **except for the alkali metals and alkaline earth metals**.
- When a solution contains both cations and anions from weak acids and bases, use K_a and K_b to determine the final pH of the solution.

Acid-Base Behavior and Chemical Structure

Factors that Affect Acid Strength

Consider H-X. For this substance to be an acid we need:

- H-X bond to be polar with Hδ+ and Xδ- (if X is a metal then the bond polarity is Hδ-, Xδ+ and the substance is a base),
- the H-X bond must be weak enough to be broken,
- the conjugate base, X^-, must be stable.

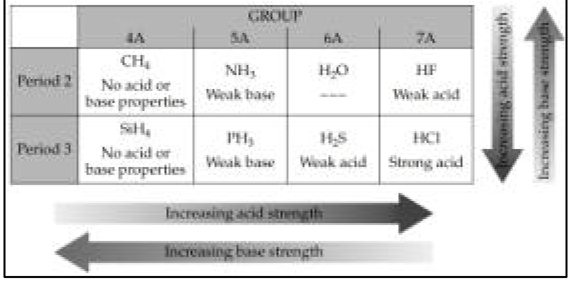
Acid-Base Behavior and Chemical Structure

Binary Acids

- Acid strength increases across a period and down a group.
- Conversely, base strength decreases across a period and down a group.
- HF is a weak acid because the bond energy is high.
- The electronegativity difference between C and H is so small that the C-H bond is non-polar and CH_4 is neither an acid nor a base.

Acid-Base Behavior and Chemical Structure

Binary Acids



	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

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Acid-Base Behavior and Chemical Structure

Oxyacids

- Oxyacids contain O-H bonds.
- All oxyacids have the general structure Y-O-H.
- The strength of the acid depends on Y and the atoms attached to Y.
  - If Y is a metal (low electronegativity), then the substances are bases.
  - If Y has intermediate electronegativity (e.g. I, EN = 2.5), the electrons are between Y and O and the substance is a weak oxyacid.

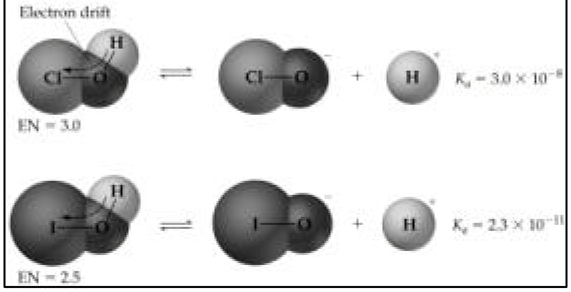
Acid-Base Behavior and Chemical Structure

Oxyacids

- If Y has a large electronegativity (e.g. Cl, EN = 3.0), the electrons are located closer to Y than O and the O-H bond is polarized to lose H^+.
- The number of O atoms attached to Y increase the O-H bond polarity and the strength of the acid increases (e.g. HOCl is a weaker acid than $HClO_2$ which is weaker than $HClO_3$ which is weaker than $HClO_4$ which is a strong acid).

Acid-Base Behavior and Chemical Structure

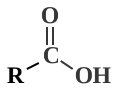
Oxyacids



Acid-Base Behavior and Chemical Structure

Carboxylic Acids

- Carboxylic acids all contain the COOH group.
- All carboxylic acids are weak acids.
- When the carboxylic acid loses a proton, it generate the carboxylate anion, COO^-.



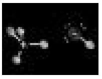
Lewis Acids and Bases

- Brønsted-Lowry acid is a proton donor.
- Focusing on electrons: a Brønsted-Lowry acid can be considered as an electron pair acceptor.
- Lewis acid: electron pair acceptor.
- Lewis base: electron pair donor.
- Note: Lewis acids and bases do not need to contain protons.
- Therefore, the Lewis definition is the most general definition of acids and bases.

Lewis Acids and Bases

- Lewis acids generally have an incomplete octet (e.g. BF_3).
- Transition metal ions are generally Lewis acids.
- Lewis acids must have a vacant orbital (into which the electron pairs can be donated).
- Compounds with π-bonds can act as Lewis acids:

$$H_2O(l) + CO_2(g) \rightarrow H_2CO_3(aq)$$



Lewis Acids and Bases

Hydrolysis of Metal Ions

- Metal ions are positively charged and attract water molecules (via the lone pairs on O).
- The higher the charge, the smaller the metal ion and the stronger the M-OH_2 interaction.
- Hydrated metal ions act as acids:

$$Fe(H_2O)_6{}^{3+}(aq) \rightleftharpoons Fe(H_2O)_5(OH)^{2+}(aq) + H^+(aq)$$

$K_a = 2 \text{ x } 10^{-3}$

- The pH increases as the size of the ion increases (e.g. Ca^{2+} vs. Zn^{2+}) and as the charge increases (Na^+ vs. Ca^{2+} and Zn^{2+} vs. Al^{3+}).

Lewis Acids and Bases

Hydrolysis of Metal Ions