Ch 15 Acid/Base Equilibrium and pH

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Acid/Base Definitions

- Arrhenius Model
  - Acids produce hydrogen ions in aqueous solutions, HCl
  - Bases produce hydroxide ions in aqueous solutions, NaOH

Based on H+ and OH-

- Bronsted-Lowry Model
  - Acids are proton donors
  - Bases are proton acceptors

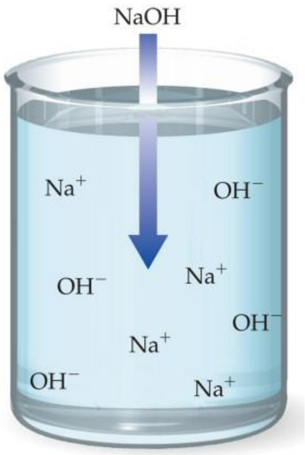
Based on reactions in which H+ is transferred

- Lewis Acid Model
  - Acids are electron pair acceptors
  - Bases are electron pair donors

Arrhenius Theory

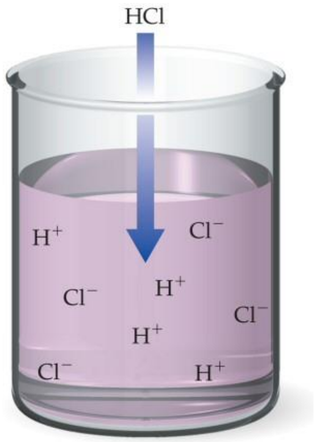
- bases **dissociate** in water to produce OH^- ions and cations
  - ionic substances dissociate in water

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



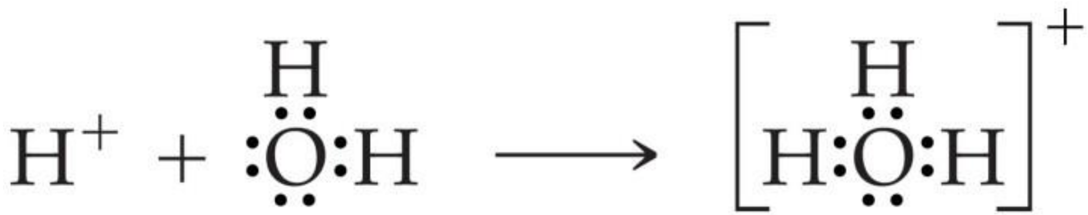
- acids **ionize** in water to produce H^+ ions and anions
  - because molecular acids are not made of ions, they cannot dissociate
  - they must be pulled apart, or **ionized**, by the water

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



Problems with Arrhenius Theory

- does not explain why molecular substances, like NH_3, dissolve in water to form basic solutions – even though they do not contain $OH^–$ ions
- does not explain acid-base reactions that do not take place in aqueous solution
- H^+ ions do not exist in water. Acid solutions contain H_3O^+ ions
  - H^+ = a proton!
  - H_3O^+ = **hydronium ions**

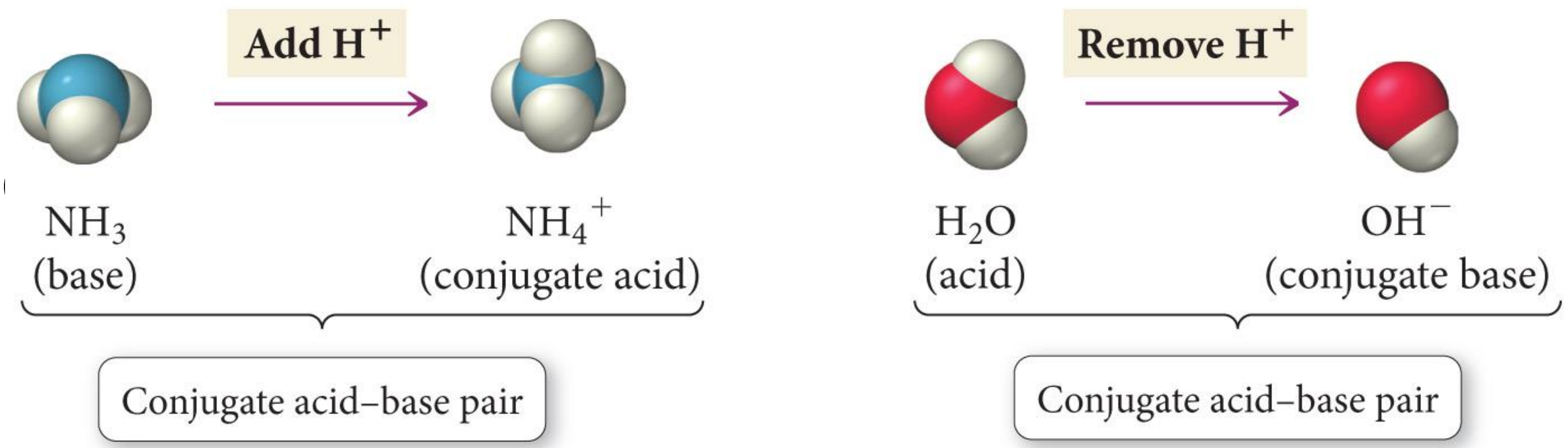


Brønsted-Lowery Theory

- in a Brønsted-Lowery Acid-Base reaction, an H^+ is transferred
  - does not have to take place in aqueous solution
  - broader definition than Arrhenius
- acid is H donor, base is H acceptor
  - base structure must contain an atom with an unshared pair of electrons
- in the reaction, the acid molecule gives an H^+ to the base molecule

$$H{-}A + :B \Leftrightarrow :A^{-} + H{-}B^{+}$$

Conjugate Acid–Base Pairs

- In a Brønsted-–Lowry acid–base reaction,
  - the original base becomes an acid in the reverse reaction.
  - the original acid becomes a base in the reverse process.
- 

Conjugate Pairs

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

Base | Acid | Conjugate acid | Conjugate base

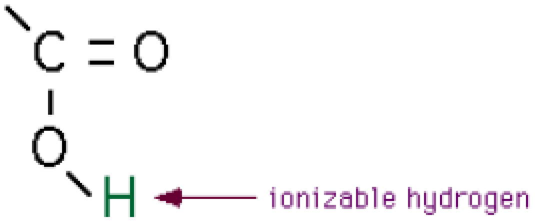
A base accepts a proton and becomes a conjugate acid.

An acid donates a proton and becomes a conjugate base.

H–A	+	:B	⇔	$:A^-$	+	$H–B^+$
acid		base		conjugate base		conjugate acid
$HCHO_2$	+	H_2O	⇔	CHO_2^-	+	H_3O^+
acid		base		conjugate base		conjugate acid

Types of Acids

- Polyprotic Acids- more than 1 acidic hydrogen (diprotic, triprotic).
- Oxyacids - Proton is attached to the oxygen of an ion.
- Organic acids contain the Carboxyl group -COOH with the H attached to O
  generally very weak.



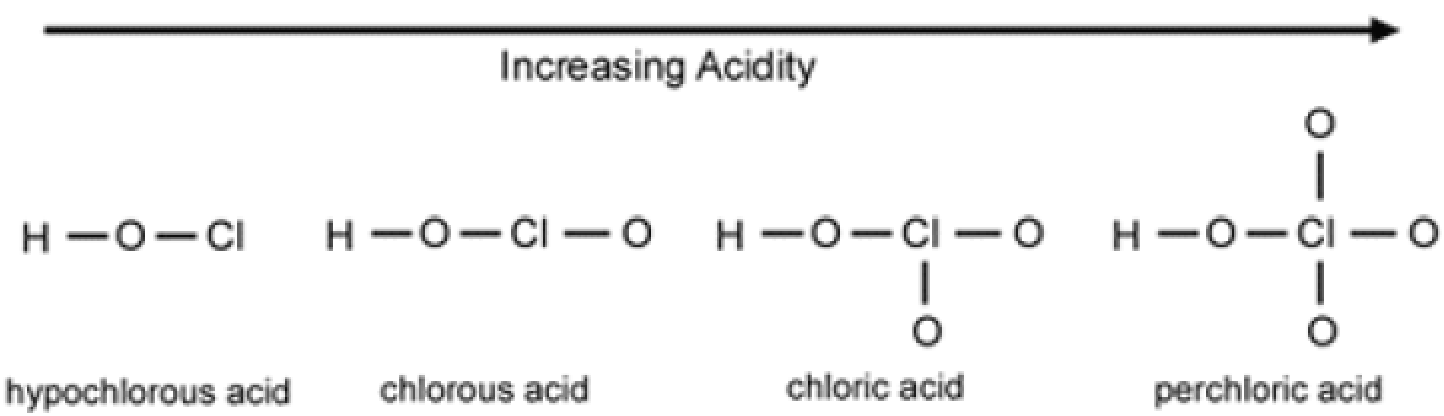
- Amphoteric Acid –
  Behave as both an acid and a base.

Strength of Acids

1. Same group, HI > HBr > HCl > HF
2. Same row, HF > H2O > NH3
3. Polyprotic Acid
   - $H_3PO_4 > H_2PO_4^- > HPO_4^{2-}$
   - $H_2SO_4 > HSO_4^-$
4. Oxyacids : $HClO_4 > HClO_3 > HClO_2 > HClO$

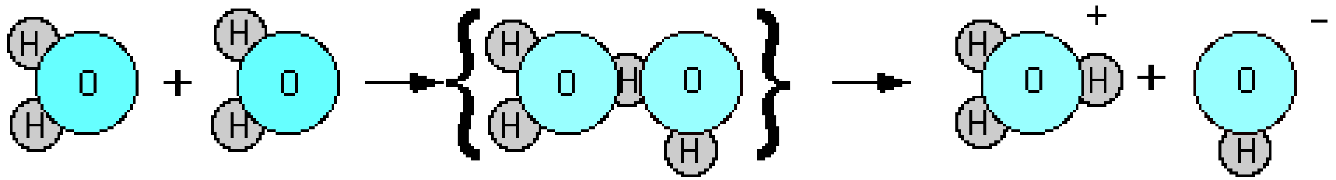
Strength of oxyacids

- The more oxygen hooked to the central atom, the more acidic the hydrogen.
- $HClO_4 > HClO_3 > HClO_2 > HClO$
- Remember that the H is attached to an oxygen atom.
- The oxygens are electronegative
- Pull electrons away from hydrogen



acid is H donor, base is H acceptor

Self-Ionization of Water



$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$$

$K = \dfrac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$ but $[H_2O]$=15.6M, a constant #

$K_w = [H_3O^+][OH^-] = 1.0x10^{-14}$ at 25C K_W is K_{water}

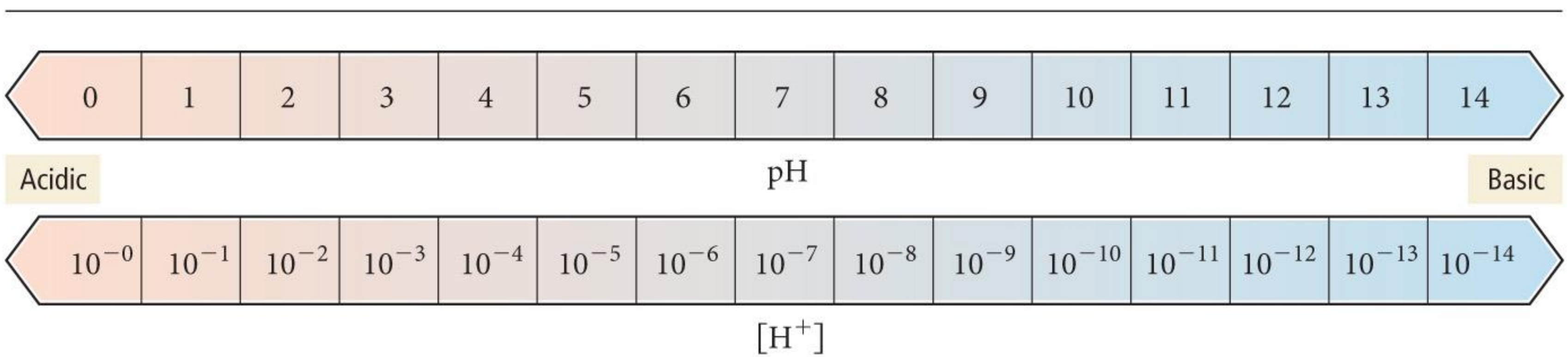
When $[H_3O^+]=[OH^-]$ in a neutral condition ,$[H^+] = [OH^-]$= 1.0 x10^{-7} M.

H_3O^+ is often written H^+ ignoring the water in equation (it is implied).

Relationships

- $K_W = [H^+][OH^-]$
- $-\log K_W = -\log([H^+][OH^-])$
- $-\log K_W = -\log[H^+] + -\log[OH^-]$
- $pK_W = pH + pOH$ $\qquad$ $pK_W = -\log K_W$
- $K_W = 1.0 \times 10^{-14}$
- **$14.00 = pH + pOH$**
- $[H^+]$, $[OH^-]$, pH and pOH Given any one of these we can find the other three.

The pH Scale



H_2O Amphoteric Acid

- Behave as both an acid and a base.
- Water autoionizes
- $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
- $K_W = [H_3O^+][OH^-] = [H^+][OH^-]$
- At 25ºC $K_W = 1.0 \times 10^{-14}$
- In EVERY aqueous solution.
- Neutral solution $[H^+] = [OH^-] = 1.0 \times 10^{-7}$
- Acidic solution $[H^+] > [OH^-]$
- Basic solution $[H^+] < [OH^-]$

pH and pOH Calculations

H^+ → OH^-: $[OH^-] = \frac{1 \times 10^{-14}}{[H^+]}$

OH^- → H^+: $[H^+] = \frac{1 \times 10^{-14}}{[OH^-]}$

H^+ → pH: $pH = -\log[H^+]$

pH → H^+: $[H^+] = 10^{-pH}$

OH^- → pOH: $pOH = -\log[OH^-]$

pOH → OH^-: $[OH^-] = 10^{-pOH}$

pH → pOH: $pOH = 14 - pH$

pOH → pH: $pH = 14 - pOH$

$[H^+]$	$[OH^-]$	pH	pOH	acidic or basic?
5.6×10^{-4}	1.8×10^{-11}	3.25	10.75	ACID
2.5×10^{-2}	4.0×10^{-13}	1.60	12.40	ACID
1.4×10^{-10}	7.1×10^{-5}	9.85	4.15	BASE

Example 15.2 Using K_w in Calculations

Calculate $[OH^-]$ at 25 °C for each solution and determine if the solution is acidic, basic, or neutral.

a. $[H_3O^+] = 7.5 \times 10^{-5}$ M **b.** $[H_3O^+] = 1.5 \times 10^{-9}$ M

Solution

a.

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

$$(7.5 \times 10^{-5})[OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{7.5 \times 10^{-5}} = 1.3 \times 10^{-10}\ \text{M}$$

Acidic solution

b.

$$(1.5 \times 10^{-9})[OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-9}} = 6.7 \times 10^{-6}\ \text{M}$$

Basic solution

Example - Calculate the pH of a 0.0010 M $Ba(OH)_2$ solution & determine if is acidic, basic or neutral

$Ba(OH)_2 = Ba^{2+} + 2\ OH^-$ therefore

$[OH^-] = 2 \times 0.0010 = 0.0020 = 2.0 \times 10^{-3}$ M

$$[H^+] = \frac{1 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12} M$$

$pH = -\log [H^+] = -\log (5.0 \times 10^{-12})$

$pH = 11.3$

pH > 7 therefore **basic**

Acid dissociation constant K_a

- The equilibrium constant for the general equation.
- $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

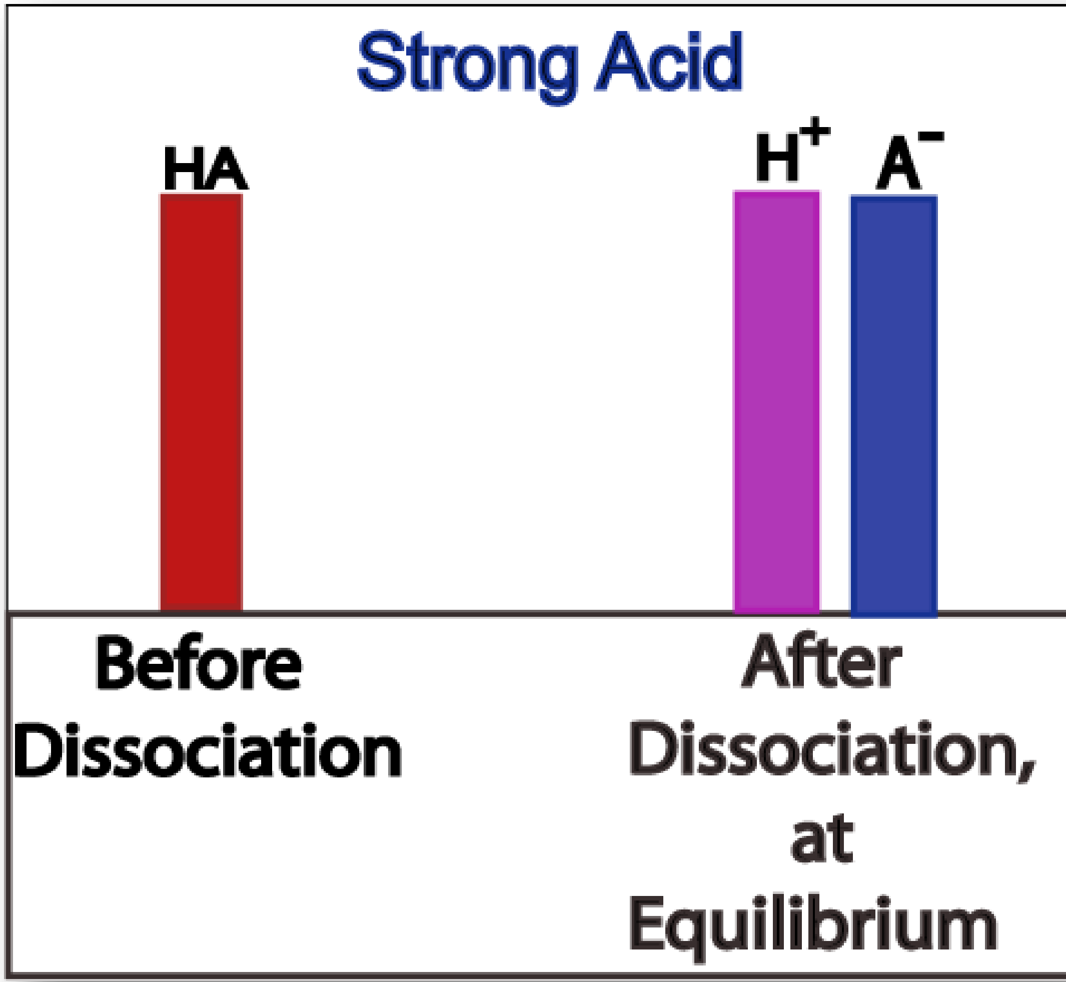
$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$ but $[H_2O]$=15.6M, a constant #

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

- H_3O^+ is often written H^+ ignoring the water in equation (it is implied).

Dissociation of Strong Acids

Strong acids are assumed to dissociate completely in solution.



Large K_a or small K_a?

Reactant favored or product favored?

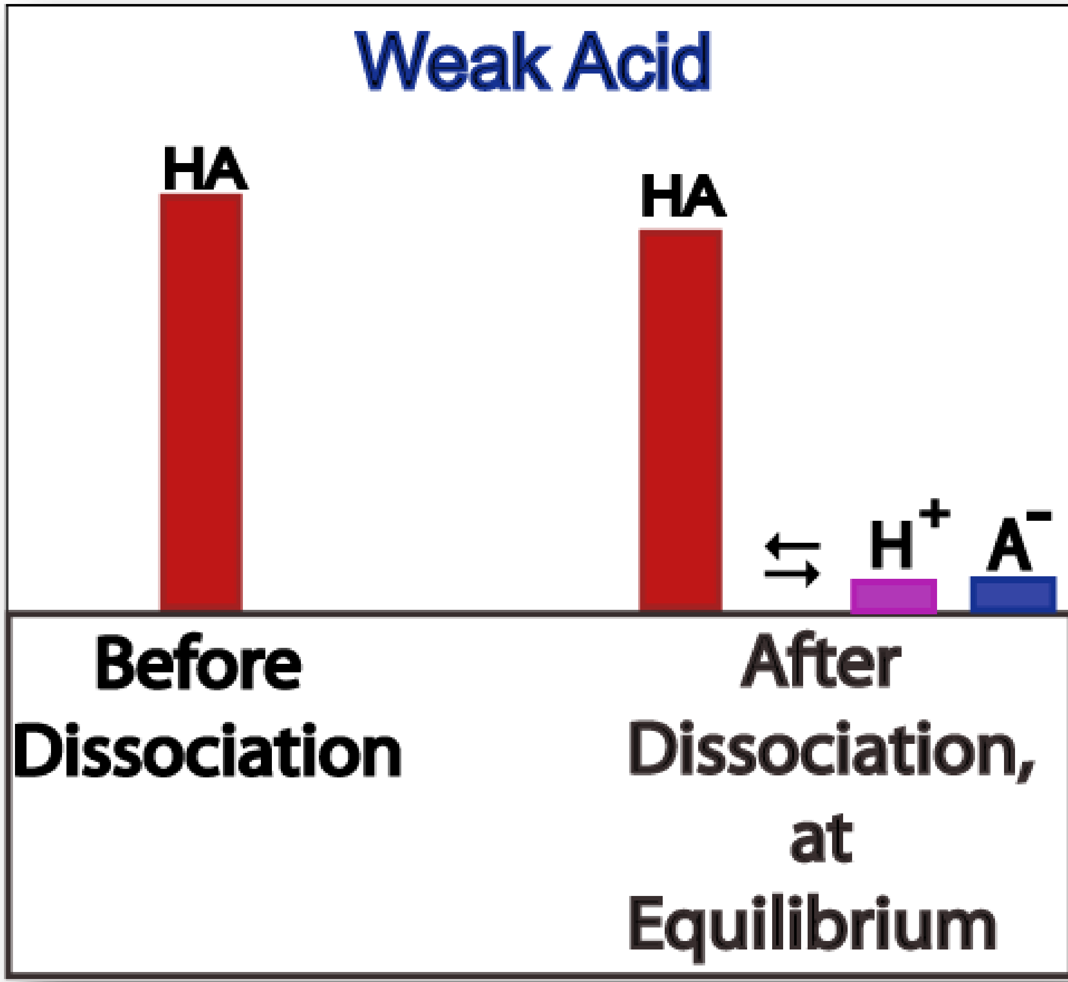
Dissociation Constants: Strong Acids

Acid	Formula	Conjugate Base	K_a
Perchloric	$HClO_4$	ClO_4^-	Very large
Hydriodic	HI	I^-	Very large
Hydrobromic	HBr	Br^-	Very large
Hydrochloric	HCl	Cl^-	Very large
Nitric	HNO_3	NO_3^-	Very large
Sulfuric	H_2SO_4	HSO_4^-	Very large
Hydronium ion	H_3O^+	H_2O	1.0

- A 0.10 M solution of HCl has $[H^+] = 0.10$ M, so the pH of the solution is 1.00

Dissociation of Weak Acids

Weak acids are assumed to dissociate only slightly (less than 5%) in solution.



Large K_a or small K_a?

Reactant favored or product favored?

Ka will be small

Dissociation Constants: Weak Acids

Acid	Formula	Conjugate Base	K_a
Iodic	HIO_3	IO_3^-	1.7×10^{-1}
Oxalic	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}
Sulfurous	H_2SO_3	HSO_3^-	1.5×10^{-2}
Phosphoric	H_3PO_4	$H_2PO_4^-$	7.5×10^{-3}
Citric	$H_3C_6H_5O_7$	$H_2C_6H_5O_7^-$	7.1×10^{-4}
Nitrous	HNO_2	NO_2^-	4.6×10^{-4}
Hydrofluoric	HF	F^-	3.5×10^{-4}
Formic	$HCOOH$	$HCOO^-$	1.8×10^{-4}
Benzoic	C_6H_5COOH	$C_6H_5COO^-$	6.5×10^{-5}
Acetic	CH_3COOH	CH_3COO^-	1.8×10^{-5}
Carbonic	H_2CO_3	HCO_3^-	4.3×10^{-7}
Hypochlorous	$HClO$	ClO^-	3.0×10^{-8}
Hydrocyanic	HCN	CN^-	4.9×10^{-10}

A Weak Acid Equilibrium Problem

What is the pH of a 0.50 M solution of acetic acid, $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$?

Step #1: Write the dissociation equation

$$HC_2H_3O_2 \leftrightarrows C_2H_3O_2^- + H^+$$

A Weak Acid Equilibrium Problem

What is the pH of a 0.50 M solution of acetic acid, $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$?

Step #2: ICE it!

$$HC_2H_3O_2 \leftrightarrows C_2H_3O_2^- + H^+$$

I	0.50	0	0
C	- x	+x	+x
E	0.50 - x	x	x

A Weak Acid Equilibrium Problem

What is the pH of a 0.50 M solution of acetic acid, $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$?

Because the right side of this equation is not a perfect square, we must put the equation into the standard quadratic form, $ax^2 + bx + c = 0$, and then solve for x using the quadratic formula (Appendix A.4):

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Step #3: Set up the law of mass action

$$HC_2H_3O_2 \leftrightarrows C_2H_3O_2^- + H^+$$

	$HC_2H_3O_2$	$C_2H_3O_2^-$	H^+
E	0.50 - x	x	x

$$1.8x10^{-5} = \frac{(x)(x)}{(0.50-x)} \cong \frac{x^2}{(0.50)}$$

Assuming X is going to be small and ignoring it in relation to 0.5

The rule of thumb is that **if** the value of X is less than 5% of all the other concentrations, p416

A Weak Acid Equilibrium Problem

What is the pH of a 0.50 M solution of acetic acid, $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$?

Step #4: Solve for x, which is also $[H^+]$

$$HC_2H_3O_2 \leftrightarrows C_2H_3O_2^- + H^+$$

E	0.50 - x	x	x

$$1.8 x 10^{-5} = \frac{x^2}{(0.50)}$$

$X = [H^+] = 3.0 \times 10^{-3}$ M

Is x / 0.5 = 6.0×10^{-3} less than 5% ? Yes ! Then our assumption was valid.

A Weak Acid Equilibrium Problem

What is the pH of a 0.50 M solution of acetic acid, $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$?

Step #5: Convert $[H^+]$ to pH

$$HC_2H_3O_2 \leftrightarrows C_2H_3O_2^- + H^+$$

	$HC_2H_3O_2$	$C_2H_3O_2^-$	H^+
E	0.50 - x	x	x

$$pH = -\log(3.0\,x10^{-5}) = 4.52$$

$$\text{Percent Ionization \%} = \frac{[H^+]_{eq}}{[HA]} x100\% = 0.6\ \%$$

percentage of acid molecules that ionize when dissolved in water; this is called the **percent ionization**.

Example 15.6 Finding the pH of a Weak Acid Solution

Find the pH of a 0.200 M HNO_2 solution.

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

	$[HNO_2]$	$[H_3O^+]$	$[NO_2^-]$
Initial	0.200	≈ 0.00	0.00
Change	$-x$	$+x$	$+x$
Equil	$0.200 - x$	x	x

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

$$= \frac{x^2}{0.200 - x} \quad (x \text{ is small})$$

$$4.6 \times 10^{-4} = \frac{x^2}{0.200}$$

$$\sqrt{4.6 \times 10^{-4}} = \sqrt{\frac{x^2}{0.200}}$$

$$x = \sqrt{(0.200)(4.6 \times 10^{-4})}$$

$$= 9.6 \times 10^{-3}$$

$$\frac{9.6 \times 10^{-3}}{0.200} \times 100\% = 4.8\%$$

Confirm that the x is small approximation is valid by calculating the ratio of x to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

$$[H_3O^+] = 9.6 \times 10^{-3}\,M$$

$$pH = -\log [H_3O^+]$$

$$= -\log (9.6 \times 10^{-3})$$

$$= 2.02$$

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{(9.6 \times 10^{-3})^2}{0.200}$$

$$= 4.6 \times 10^{-4}$$

Polyprotic Weak Acids

- Acids containing **more than one** ionizable hydrogen are called polyprotic.
  - The anion formed in one step produces another H^+ in a successive ionization step
  - The equilibrium constant becomes **smaller** with each successive step

Triprotic Acid

- Phosphoric acid
  - $H_3PO_4\,(aq) \rightleftharpoons H^+\,(aq) + H_2PO_4^-\,(aq)$ K_{a1}
  - $H_2PO_4^-\,(aq) \rightleftharpoons H^+\,(aq) + HPO_4^{2-}\,(aq)$ K_{a2}
  - $HPO_4^{2-}\,(aq) \rightleftharpoons H^+\,(aq) + PO_4^{3-}\,(aq)$ K_{a3}
  - $K_{a1} > K_{a2} > K_{a3}$
  - With each successive step, ***the acid becomes progressively weaker***

Consider the diprotic acid, sulfurous acid: H_2SO_3 $K_{a1} = 1.2 \times 10^{-2}$ $K_{a2} = 6.6 \times 10^{-8}$

a. Write the equations for the step-wise dissociation of sulfurous acid.

$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$ $K_{a1} = 1.2 \times 10^{-2}$

$HSO_3^- \rightleftharpoons H^+ + SO_3^-$ $K_{a2} = 6.6 \times 10^{-8}$

b. Calculate the pH of a 0.100 M solution of

Strength of Strong Bases

$$MOH(s) \rightarrow M^+(aq) + OH^-(aq)$$

- Strong bases are metallic hydroxides
  - Group I hydroxides (LiOH,NaOH, KOH)
  - Group II hydroxides(Ca, Ba, Mg, Sr)
  - Ph or pOH of strong bases is calculated directly from th concentration of the base in solution. See next slide

1. KH > NaH > LiH
2. $Ba(OH)_2 > Sr(OH)_2 > Ca(OH)_2 > Mg(OH)_2$

Example 15.11 Finding the [OH⁻] and pH of a Strong Base Solution

What is the OH^- concentration and pH in each solution?

a. 0.225 M KOH **b.** 0.0015 M $Sr(OH)_2$

Solution

a.

$$KOH(aq) \longrightarrow K^+(aq) + OH^-(aq)$$
$$[OH^-] = 0.225 \text{ M}$$

$$[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14}$$
$$[H_3O^+](0.225) = 1.0 \times 10^{-14}$$
$$[H_3O^+] = 4.\underline{4}4 \times 10^{-14} \text{ M}$$

$$pH = -\log[H_3O^+] = -\log(4.44 \times 10^{-14}) = 13.35$$

$$Sr(OH)_2(aq) \longrightarrow Sr^{2+}(aq) + 2\,OH^-(aq)$$
$$[OH^-] = 2(0.0015) \text{ M} = 0.0030 \text{ M}$$

$$[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14}$$
$$[H_3O^+](0.0030) = 1.0 \times 10^{-14}$$
$$[H_3O^+] = 3.3 \times 10^{-12} \text{ M}$$

$$pH = -\log[H_3O^+] = -\log(3.3 \times 10^{-12}) = 11.48$$

EXAMPLE 13.3 GRADED

Consider barium hydroxide, $Ba(OH)_2$, a white, powdery substance. Student A prepares a solution of $Ba(OH)_2$ by dissolving 4.23 g of $Ba(OH)_2$ in enough water to make 455 mL of solution.

a What is the pH of Student A's solution?

b Student B was asked to prepare the same solution as Student A. Student B's solution had a pH of 13.51. Did Student B add more or less $Ba(OH)_2$ to his solution? How much more or less $Ba(OH)_2$ was added?

c Student C was asked to add 0.60 g of NaOH to Student A's solution. What is the pH of Student C's solution? (Assume no volume change.)

(a) STUDENT A

ANALYSIS

Information given:	mass $Ba(OH)_2$ (4.23 g); volume of solution (455 mL)
Information implied:	molar mass of $Ba(OH)_2$; K_w
Asked for:	pH of the solution

STRATEGY

1. Start by expressing the concentration in g $Ba(OH)_2$/L of solution.
2. Follow the following pathway:

$$\text{mass Ba(OH)}_2/\text{L} \xrightarrow{\text{MM}} [\text{Ba(OH)}_2] \xrightarrow{2[\text{OH}^-]/[\text{Ba(OH)}_2]} [\text{OH}^-] \xrightarrow{K_w} [\text{H}^+] \xrightarrow{\text{Eq. 13.3}} \text{pH}$$

SOLUTION

$[OH^-]$	$\frac{4.23\text{ g Ba(OH)}_2}{0.455\text{ L}} \times \frac{1\text{ mol Ba(OH)}_2}{171.3\text{ g}} \times \frac{2\text{ mol OH}^-}{1\text{ mol Ba(OH)}_2} = 0.109\text{ mol/L} = 0.109\ M$
$[H^+]$	$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{0.109} = 9.2 \times 10^{-14}\ M$
pH	$\text{pH} = -\log_{10}(9.2 \times 10^{-14}) = 13.04$

How about pOH ?

Reaction of Weak Bases with Water

The generic reaction for a base reacting with water, producing its conjugate acid and hydroxide ion:

$$B + H_2O \leftrightarrows BH^+ + OH^-$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

(Yes, all weak bases do this)

K_b for Some Common Weak Bases

Many students struggle with identifying weak bases and their conjugate acids.What patterns do you see that may help you?

Base	Formula	Conjugate Acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	$CH_3NH_3^+$	4.38×10^{-4}
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	5.6×10^{-4}
Diethylamine	$(C_2H_5)_2NH$	$(C_2H_5)_2NH_2^+$	1.3×10^{-3}
Triethylamine	$(C_2H_5)_3N$	$(C_2H_5)_3NH^+$	4.0×10^{-4}
Hydroxylamine	$HONH_2$	$HONH_3^+$	1.1×10^{-8}
Hydrazine	H_2NNH_2	$H_2NNH_3^+$	3.0×10^{-6}
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	3.8×10^{-10}
Pyridine	C_5H_5N	$C_5H_5NH^+$	1.7×10^{-9}

Reaction of Weak Bases with Water

The base reacts with water, producing its conjugate acid and hydroxide ion:

$CH_3NH_2 + H_2O \leftrightarrows CH_3NH_3^+ + OH^-$

$K_{base} = K_b = 4.38 \times 10^{-4}$

$$K_b = 4.38\,x10^{-4} = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

A Weak Base Equilibrium Problem

What is the pH of a 0.50 M solution of ammonia, NH_3, $K_b = 1.8 \times 10^{-5}$?

Step #1: Write the equation for the reaction

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

A Weak Base Equilibrium Problem

What is the pH of a 0.50 M solution of ammonia, NH_3, $K_b = 1.8 \times 10^{-5}$?

Step #2: ICE it!

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

I	0.50	0	0
C	- x	+x	+x
E	0.50 - x	x	x

A Weak Base Equilibrium Problem

What is the pH of a 0.50 M solution of ammonia, NH_3, $K_b = 1.8 \times 10^{-5}$?

Step #3: Set up the law of mass action

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

E	0.50 - x	x	x

$$1.8x10^{-5} = \frac{(x)(x)}{(0.50 - x)} \cong \frac{x^2}{(0.50)}$$

A Weak Base Equilibrium Problem

What is the pH of a 0.50 M solution of ammonia, NH_3, $K_b = 1.8 \times 10^{-5}$?

Step #4: Solve for x, which is also $[OH^-]$

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

E	0.50 - x	x	x

$$1.8\,x10^{-5} = \frac{x^2}{(0.50)}$$

$[OH^-] = 3.0 \times 10^{-3}$ M

A Weak Base Equilibrium Problem

What is the pH of a 0.50 M solution of ammonia, NH_3, $K_b = 1.8 \times 10^{-5}$?

Step #5: Convert $[OH^-]$ to pH

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

E	0.50 - x	x	x

$$pOH = -\log(3.0\,x10^{-5}) = 4.52$$

$$pH = 14.00 - pOH = 9.48$$

Relationship Between Ka and Kb

Relation between K_a and K_b

- Consider the relation between a conjugate acid-base pair
  - $HB\ (aq) \rightleftharpoons H^+\ (aq) + B^-\ (aq)$ $K_I = K_a$ of HB
  - $B^-\ (aq) + H_2O \rightleftharpoons HB\ (aq) + OH^-\ (aq)$ $K_{II} = K_b$ of B^-
- These add to
  - $H_2O \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$ $K_{III} = K_w$
- Since $K_I K_{II} = K_{III}$, **$K_a K_b = K_w = 1.0 \times 10^{-14}$**
  - for a conjugate acid base pair only
  - In log form, **$pK_a + pK_b = pK_w = 14.00$**

- K_a and K_b are inversely related
  - The larger K_a is, the smaller K_b is.

Relationship between Strengths of Acids and their Conjugate Bases

- the stronger an acid is, the weaker the attraction of the ionizable H for the rest of the molecule is
- the better the acid is at donating H, the worse its conjugate base will be at accepting a H

strong acid HCl + $H_2O \rightarrow Cl^- + H_3O^+$ weak conj. base

weak acid HF + $H_2O \Leftrightarrow F^- + H_3O^+$ strong conj. base

Weak Bases and their Equilibrium Expressions

- Types of weak bases
  - **Molecules**
    - Ammonia, NH_3, and amines
    - $NH_3\,(aq) + H_2O \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$
  - **Anions**
    - Anions derived from weak acids are weak bases
    - $I^-\,(aq) + H_2O \rightleftharpoons HI\,(aq) + OH^-\,(aq)$

EXAMPLE 13.10

Write an equation to explain why each of the following produces a basic water solution.

(a) NO_2^- (b) Na_2CO_3 (c) $KHCO_3$

STRATEGY

1. React each basic anion with a water molecule.
2. The weak base picks up the proton (H^+) and increases its charge by one unit to create its conjugate acid.
3. OH^- is the other product of the reaction.

SOLUTION

(a) $NO_2^-(aq) + H_2O \rightarrow HNO_2^{-1+1}(aq) + OH^-(aq) \rightarrow HNO_2(aq) + OH^-(aq)$

HOH

(b) $CO_3^{2-}(aq) + H_2O \rightarrow HCO_3^{-2+1}(aq) + OH^-(aq) \rightarrow HCO_3^-(aq) + OH^-(aq)$

HOH

(c) $HCO_3^-(aq) + H_2O \rightarrow HHCO_3^{-1+1}(aq) + OH^-(aq) \rightarrow H_2CO_3(aq) + OH^-(aq)$

HOH

Acid-Base Properties of Salts

Acid-Base Properties of Solutions of Salts

- A salt is an **ionic solid** containing a cation other than H^+ and an anion other than OH^- or O^{2-}.

Solutions of many salts are neutral in pH.

Solutions of many other salts are acidic or basic.

If the cation can form weak base, the salt solution will be acidic.

If the anion can form weak acid, the salt solution will be basic.

strong acid $HCl + H_2O \rightarrow Cl^- + H_3O^+$ weak conj. base

weak acid $HF + H_2O \Leftrightarrow F^- + H_3O^+$ strong conj. base

Acid-Base Properties of Salts

Salts with Acidic and Basic ions

1. IF K_a for the acidic ion is greater than K_b for the basic ion, the solution is acidic
2. IF K_b for the basic ion is greater than K_a for the acidic ion, the solution is basic
3. IF K_b for the basic ion is equal to K_a for the acidic ion, the solution is neutral

NH4F because HF is a stronger acid than NH4+, Ka of NH4+ is larger than Kb of the F−; therefore, the solution will be acidic. Ka >Kb , acidic solution

For each solution, state whether it would be Acidic, Basic, or Neutral.

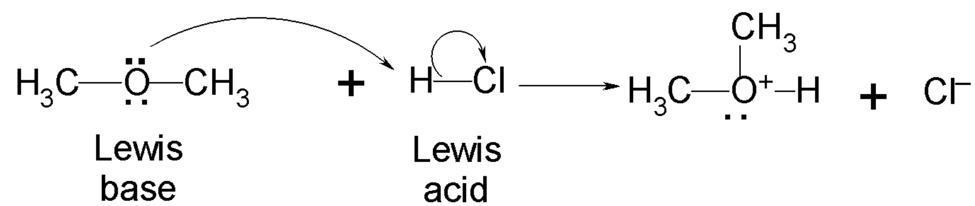
ACID NH_4Cl (WB SA)	N Na_2SO_4 (SB SA)	BASE $KC_2H_3O_2$ (SB WA)
BASIC CaF_2 (SB WA)	B $MgSO_3$ (SB WA)	NEUTRAL KI (SB SA)

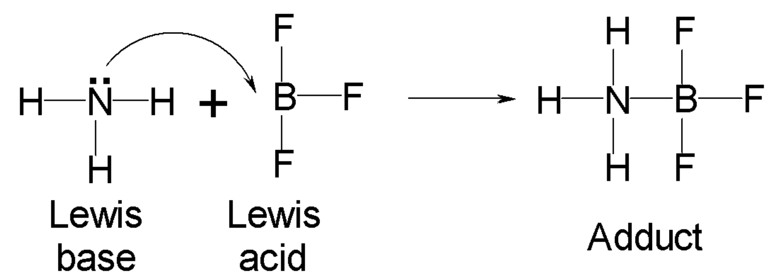
Classifying Salt Solutions as Acidic, Basic, or Neutral

- If the salt cation is the counterion of a strong base and the anion is the conjugate base of a strong acid, it will form a neutral solution.
  - NaCl $Ca(NO_3)_2$ KBr
- If the salt cation is the counterion of a strong base and the anion is the conjugate base of a weak acid, it will form a basic solution.
  - NaF $Ca(C_2H_3O_2)_2$ KNO_2
- If the salt cation is the conjugate acid of a weak base and the anion is the conjugate base of a strong acid, it will form an acidic solution.
  - NH_4Cl
- If the salt cation is a highly charged metal ion and the anion is the conjugate base of a strong acid, it will form an acidic solution.
  - $Al(NO_3)_3$

Lewis Acids and Bases

- Most general definition.
- Acids are electron pair acceptors.
- Bases are electron pair donors.





Consider the reaction: $F^- + H_2O \leftrightharpoons HF + OH^-$

F- would be a (circle all answers that apply):

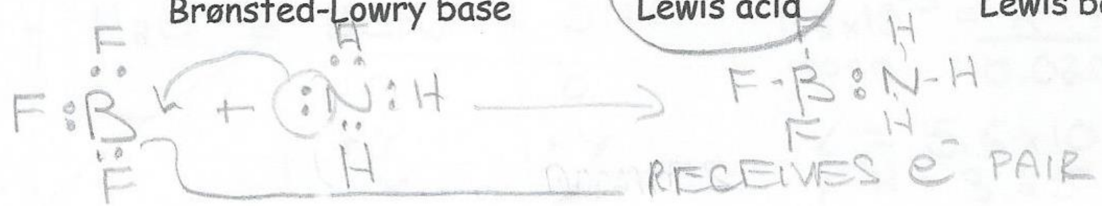
Brønsted-Lowry acid | Brønsted-Lowry base | Lewis acid | Lewis base

NO HYDROGENS DONATED OR RECEIVED
DOES NOT

Consider the reaction: $BF_3 + NH_3 \rightarrow BF_3NH_3$

BF_3 would be a (circle all answers that apply):

Brønsted-Lowry acid | Brønsted-Lowry base | Lewis acid | Lewis base



Acid-Base Properties of Neutral Salts

A. Salts That Produce Neutral Solutions
   1. Salts that consist of the cations of strong bases and the anions of strong acids have no effect on pH, ($[H^+]$), when dissolved in water
   2. Cations of strong bases
      a. Na^+ K^+ (Group 1A)
   3. Anions of strong acids
      a. Cl^-, NO_3^-

Type of Salt	Examples	Comment	pH of solution
Cation is from a strong base, anion from a strong acid	KCl, KNO_3 $NaCl$ $NaNO_3$	Both ions are neutral	Neutral

These salts simply dissociate in water:

$$KCl(s) \rightarrow K^+(aq) + Cl^-(aq)$$

Acid-Base Properties of Basic Salts

Salts that Produce Basic Solutions

1. For any salt whose cation has neutral properties and whose anion is the conjugate base of a weak acid, the aqueous solution will be basic

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

base *acid* *acid* *base*

Type of Salt	Examples	Comment	pH of solution
Cation is from a strong base, anion from a weak acid	$NaC_2H_3O_2$ KCN, NaF	Cation is neutral, Anion is basic	Basic

The basic anion can accept a proton from water:

$$C_2H_3O_2^- + H_2O \leftrightarrows HC_2H_3O_2 + OH-$$

base *acid* *acid* *base*

$C_2H_3O_2^-$ anion is Basic Salt !

Acid-Base Properties of Acid Salts

Salts that Produce Acidic Solutions

1. Salts in which the anion is not a base and the cation is the conjugate acid acid of a weak base produce acid solutions

   $NH_4^+(aq)$ • • $NH_3(aq)$ + $H^+(aq)$

2. Salts that possess a highly charged metallic ion, such as Al^{3+}
   a. Aluminum ion in water is hydrated, $Al(H_2O)_6^{3+}$
   b. High metallic charge polarizes O - H bond in water
   c. Hydrogens in water become acidic

Type of Salt	Examples	Comment	pH of solution
Cation is the conjugate acid of a weak base, anion is from a strong acid	NH_4Cl, NH_4NO_3	Cation is acidic, Anion is neutral	Acidic

The acidic cation NH_4^+ can act as a proton donor:

$NH_4^+(aq) \leftrightarrows NH_3(aq) + H^+(aq)$

Acid Salt conjugate base Proton

Acid-Base Properties of Meal Salts

Type of Salt	Examples	Comment	pH of solution
Cation is a highly charged metal ion; Anion is from strong acid	$Al(NO_3)_2$ $FeCl_3$	Hydrated cation acts as an acid; Anion is neutral	Acidic

Step #1:

$AlCl_3(s) + 6H_2O \rightarrow Al(H_2O)_6^{3+}(aq) + Cl^-(aq)$

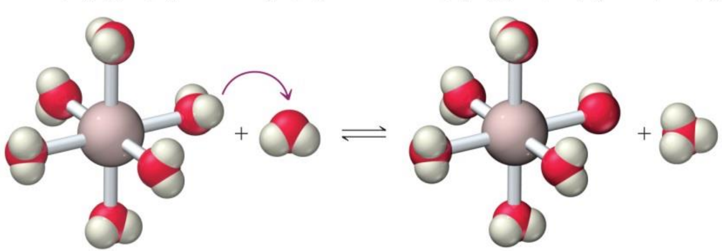
Salt water Complex ion anion

Step #2:

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

Acid Conjugate base Proton

$Al(H_2O)_6^{3+}(aq) + H_2O(aq) \rightleftharpoons Al(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$



Metal Cations as Weak Acids

Acid-Base Properties of Salts

Salts with Acidic and Basic ions

1. IF K_a for the acidic ion is greater than K_b for the basic ion, the solution is acidic
2. IF K_b for the basic ion is greater than K_a for the acidic ion, the solution is basic
3. IF K_b for the basic ion is equal to K_a for the acidic ion, the solution is neutral

Type of Salt	Examples	Comment	pH of solution
Cation is the conjugate acid of a weak base, anion is conjugate base of a weak acid	$NH_4C_2H_3O_2$ NH_4CN	Cation is acidic, Anion is basic	See below