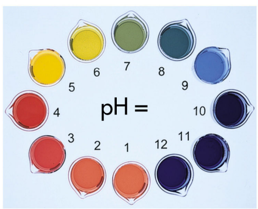
Acid-Base Chemistry

(a)

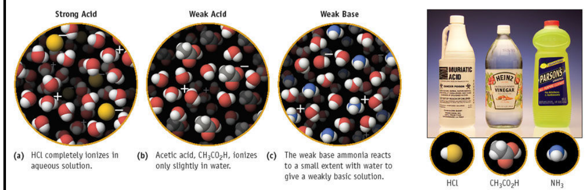


(b)

Strong vs Weak Acids and Bases

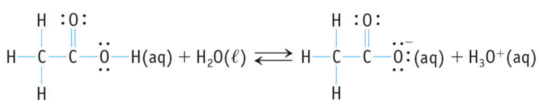
Based on the extent of ionization in solution

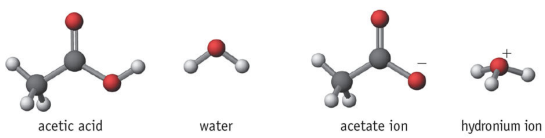
$$HCl(aq) + H_2O(\ell) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$



(a) HCl completely ionizes in aqueous solution. (b) Acetic acid, CH_3CO_2H, ionizes only slightly in water. (c) The weak base ammonia reacts to a small extent with water to give a weakly basic solution.

Weak Acid Ionization Constant





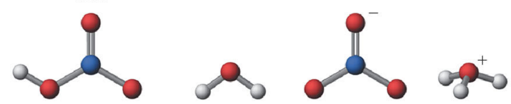
$$K = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$

Bronsted Acid

Proton Donor

$$HNO_3(aq) + H_2O(\ell) \longrightarrow NO_3^-(aq) + H_3O^+(aq)$$

Acid

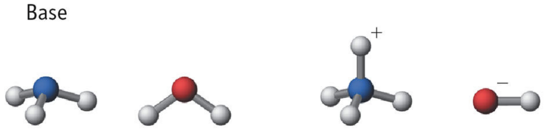


Bronsted Base

Proton Acceptor

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

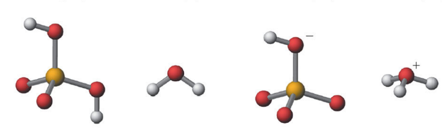
Base



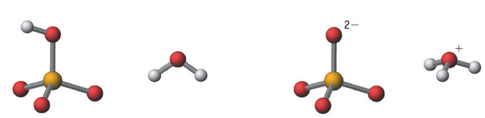
Polyprotic Acids

Capable of donating more than one proton

$$H_2SO_4(aq) + H_2O(\ell) \longrightarrow HSO_4^-(aq) + H_3O^+(aq)$$



$$HSO_4^-(aq) + H_2O(\ell) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$$



Amphiprotic **means able to act as an acid or a base [i.e. can gain or lose a proton] and** ***amphoteric*** **means able to react with an acid or a base.**

Ex. Aluminium oxide is amphoteric
in acid: $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$
in base: $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$
$NaAl(OH)_4$ is sodium aluminate

Water is both amphoteric and amphiprotic

Table 17.1 Polyprotic Acids and Bases

Acid Form	Amphiprotic Form	Base Form
H_2S (hydrosulfuric acid or hydrogen sulfide)	HS^- (hydrogen sulfide ion)	S^{2-} (sulfide ion)
H_3PO_4 (phosphoric acid)	$H_2PO_4^-$ (dihydrogen phosphate ion) HPO_4^{2-} (hydrogen phosphate ion)	PO_4^{3-} (phosphate ion)
H_2CO_3 (carbonic acid)	HCO_3^- (hydrogen carbonate ion or bicarbonate ion)	CO_3^{2-} (carbonate ion)
$H_2C_2O_4$ (oxalic acid)	$HC_2O_4^-$ (hydrogen oxalate ion)	$C_2O_4^{2-}$ (oxalate ion)

Exercise 17.1

a) Write a balanced equation for the reaction that occurs when H_3PO_4, phosphoric acid, donates a proton to water to form the dihydrogen phosphate ion. Is the dihydrogen phosphate ion an acid, a base, or amphiprotic?

b) Write a balanced equation for the reaction that occurs when the cyanide ion, CN^-, accepts a proton from water to form HCN. Is CN^- a Bronsted acid or base?

a) $H_3PO_{4(aq)} + H_2O_{(l)} \leftrightarrow H_2PO_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$

Since H_3PO_4 is a weak acid, $H_2PO_4^-$ can act as both an acid and a base (amphiprotic). It's preferred direction is going to be dependent upon the K_a value of the dihydrogen phosphate ion.

b) $CN^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow HCN_{(aq)} + OH^-{}_{(aq)}$

The CN- is acting as a Bronsted base because it is a proton acceptor.

Conjugate Acid-Base Pairs

Differ by one H⁺

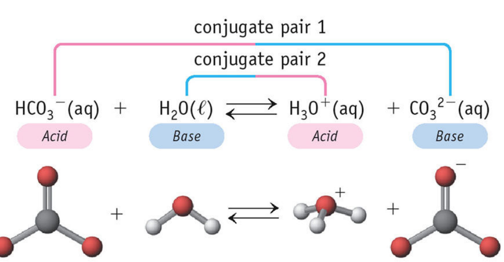


Table 17.2 Conjugate Acid–Base Pairs*

Name	Acid 1		Base 2		Base 1		Acid 2
Hydrochloric acid	HCl	+	H_2O	$\longrightarrow$	Cl^-	+	H_3O^+
Nitric acid	HNO_3	+	H_2O	$\longrightarrow$	NO_3^-	+	H_3O^+
Hydrogen carbonate	HCO_3^-	+	H_2O	$\rightleftharpoons$	CO_3^{2-}	+	H_3O^+
Acetic acid	CH_3CO_2H	+	H_2O	$\rightleftharpoons$	$CH_3CO_2^-$	+	H_3O^+
Hydrocyanic acid	HCN	+	H_2O	$\rightleftharpoons$	CN^-	+	H_3O^+
Hydrogen sulfide	H_2S	+	H_2O	$\rightleftharpoons$	HS^-	+	H_3O^+
Ammonia	H_2O	+	NH_3	$\rightleftharpoons$	OH^-	+	NH_4^+
Carbonate ion	H_2O	+	CO_3^{2-}	$\rightleftharpoons$	OH^-	+	HCO_3^-
Water	H_2O	+	H_2O	$\rightleftharpoons$	OH^-	+	H_3O^+

Exercise 17.2

In the following reaction, identify the acid on the left and its conjugate base on the right. Similarly, identify the base on the left and its conjugate acid on the right.

$$HNO_{3(aq)} + NH_{3(aq)} \leftrightarrow NH_4{}^+{}_{(aq)} + NO_3{}^-{}_{(aq)}$$

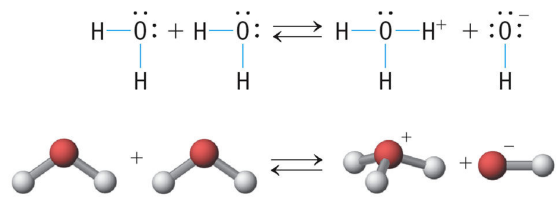
Answer

HNO_3 and $NH_4{}^+$ are acids; NH_3 and $NO_3{}^-$ are bases.

The Autoionization of Water

Pure water will autoionize to an extent that is temperature dependent

$$2\ H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$



Where Does the pH Scale Come From?

In any sample of pure water a certain number of water molecules will interact with one another

$$H_2O_{(l)} + H_2O_{(l)} \leftrightarrow H_3O^+{}_{(aq)} + OH^-{}_{(aq)}$$

This is known as the *autoionization* of water

Hydronium and hydroxide are produced in a 1:1 ratio

At 25°C, the concentration (molarity) of H_3O^+ or OH^- at any given time (in pure water) is $1.0x10^{-7}$M

The product of the concentrations is given by:

$[H_3O^+][OH^-] = [1.0x10^{-7}][1.0x10^{-7}] = 1.0x10^{-14} = K_w$

K_w = Ion product constant of water

The product of the hydronium and hydroxide ion concentration in any solution must always be K_w

Implications:

As the concentration of H_3O^+ goes up, OH^- goes down and vice versa such that the product is always K_w

Concentrations of H_3O^+ greater than $1.0x10^{-7}$ will have a pH less than 7 (given pH = $-\log[H_3O^+]$) and be acidic

Concentrations of H_3O^+ less than $1.0x10^{-7}$ will have a pH greater than 7 and be basic (alkaline)

The Variation of K_w with Temperature

°C	K_w
10	0.29×10^{-14}
15	0.45×10^{-14}
20	0.68×10^{-14}
25	1.01×10^{-14}
30	1.47×10^{-14}
50	5.48×10^{-14}

Exercise 17.3

A solution of the strong acid HCl has [HCl] = $4.0x10^{-3}$M. What are the concentrations of H_3O^+ and OH^- in this solution at 25°C?

As a strong acid, the concentration of H_3O^+ will be equal to its molarity = **$4.0x10^{-3}$M**. The hydroxide ion concentration will be $1.01x10^{-14}/4.0x10^{-3}$ = **$2.5x10^{-12}$M**

pH

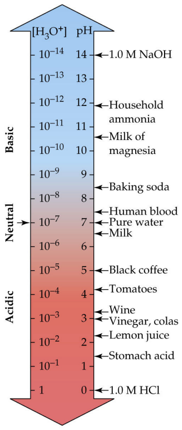
pH = The "power" of hydrogen

Related to the molarity of H^+ (H_3O^+) in solution

designated by $[H^+]$ (brackets mean molarity)

Definition: pH = -log of the hydronium ion concentration

pH = $-\log[H^+]$	$[H^+] = 10^{-pH}$
pOH = $-\log[OH^-]$	$[OH^-] = 10^{-pOH}$



Examples of the pH of common substances

NOTE: Each pH change of 1 corresponds to a ten-fold increase or decrease in the hydronium concentration.

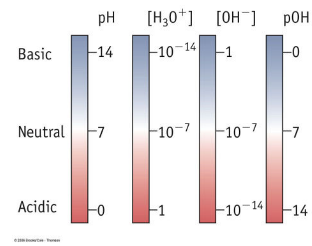
$[H_3O^+]$ =	pH =
.1	1
.01	2
.001	3
.0001	4

Mathematical Implications:

$$[H_3O^+][OH^-] = K_w = 1.0\times10^{-14}$$

$$pH + pOH = 14 = pK_w$$

(Note that acids are lower than 7 on the pH scale and higher than 7 on the pOH scale)



Exercise 17.4

a) What is the pH of a 0.0012M NaOH solution at 25°C?

b) The pH of a diet soda is 4.32 at 25°C. What are the hydronium and hydroxide ion concentrations in the soda?

c) If the pH of a solution containing the strong base $Sr(OH)_2$ is 10.46 at 25°C, what is the concentration of $Sr(OH)_2$?

Answer:
a) pH = -log(1.0x10^{-14} / 0.0012) = **11.08**
b) $[H_3O^+]$ = 10$^{-4.32}$ = **4.79x10^{-5}M** $[OH^-]$ = 1.0x10^{-14}/4.79x10^{-5} = **2.09x10^{-10}M**
c) pOH = 14.00 – 10.46 = 3.54
[OH-] = 10$^{-3.54}$ = 2.88x10^{-4}M. Since each $Sr(OH)_2$ has two hydroxides the concentration of $Sr(OH)_2$ is 2.88x10^{-4} / 2 = **1.44x10^{-4}M**

Equilibrium Constants for Acids and Bases

Weak Acid Equilibrium Constant:

$HA_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + A^-_{(aq)}$

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

Weak Base Equilibrium Constant:

$B_{(aq)} + H_2O_{(l)} \leftrightarrow BH^+_{(aq)} + OH^-_{(aq)}$

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

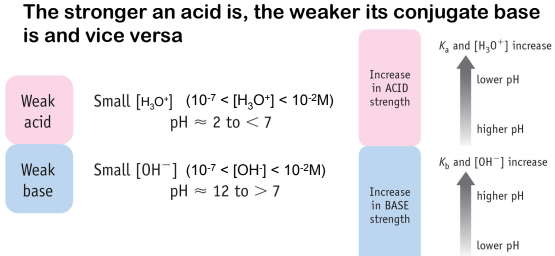
Refer to table 17.3, page 808 for K_a and K_b values

Points:

Very strong acids and bases do not have K values, as they are assumed to dissociate 100%

$K_aK_b = K_w$ for conjugate acid-base pairs

The stronger an acid is, the weaker its conjugate base is and vice versa



The salts formed from the conjugates in acid-base neutralizations can have an effect on the pH of the "neutralized" solution

A salt containing the conjugate acid of a weak base will make the solution acidic (pH<7)

A salt containing the conjugate base of a weak acid will make the solution basic (pH>7)

A salt containing the conjugates of a strong acid and base will be neutral (e.g. NaCl)

A the pH of a solution containing a salt of a weak acid and base depends on the relative K_a and K_b of the conjugates.

Salt	Resulting pH
KCl	Neutral (7)
KNO_2	Basic (>7)
NH_4Cl	Acidic (<7)

$NO_2^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow HNO_{2(aq)} + OH^-{}_{(aq)}$ (for KNO_2)

$NH_4^+{}_{(aq)} + H_2O_{(l)} \leftrightarrow NH_{3(aq)} + H_3O^+{}_{(aq)}$ (for NH_4Cl)

If both ions from the salt are from weak acids and bases, then the individual K_a and K_b values must be considered. ($K_{net} = K_w/K_aK_b$ where K_a and K_b are the equilibrium constants for the conjugates of the reactants)

Table 17.5 Characteristics of Acid–Base Reactions

Type	Example	Net Ionic Equation	Species Present After Equal Molar Amounts are Mixed; pH
Strong acid + strong base	$HCl + NaOH$	$H_3O^+(aq) + OH^-(aq) \longrightarrow 2\ H_2O(\ell)$	Cl^-, Na^+, pH = 7
Strong acid + weak base	$HCl + NH_3$	$H_3O^+(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + H_2O(\ell)$	Cl^-, NH_4^+, pH < 7
Weak acid + strong base	$HCO_2H + NaOH$	$HCO_2H(aq) + OH^-(aq) \rightleftharpoons HCO_2^-(aq) + H_2O(\ell)$	HCO_2^-, Na^+, pH > 7
Weak acid + weak base	$HCO_2H + NH_3$	$HCO_2H(aq) + NH_3(aq) \rightleftharpoons HCO_2^-(aq) + NH_4^+(aq)$	HCO_2^-, NH_4^+, pH dependent on K_a and K_b of conjugate acid and base

Exercise 17.5

Refer to table 17.3 on page 808 to answer the following:

a) Which is the stronger acid, H_2SO_4 or H_2SO_3?

b) Is benzoic acid, $C_6H_5CO_2H$, stronger or weaker than acetic acid?

c) Which has the stronger conjugate base, acetic acid or boric acid?

d) Which is the stronger base, ammonia or the acetate ion?

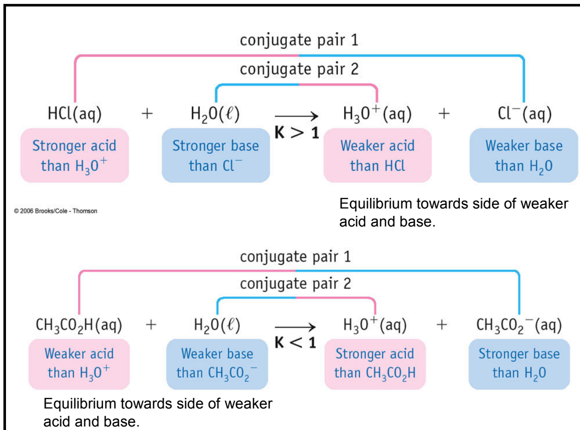
e) Which has the stronger conjugate acid, ammonia or the acetate ion?

Aqueous Solutions of Salts

Table 17.4 Acid and Base Properties of Some Ions in Aqueous Solution

	Neutral	Basic	Acidic
Anions	Cl^-, Br^-, I^-, NO_3^-, ClO_4^-	$CH_3CO_2^-$, HCO_2^-, CO_3^{2-}, S^{2-}, F^-, CN^-, PO_4^{3-}, HCO_3^-, HS^-, NO_2^-, SO_4^{2-}, HPO_4^{2-}, SO_3^{2-}, OCl^-	HSO_4^-, $H_2PO_4^-$, HSO_3^-
Cations	Li^+, Na^+, K^+, Ca^{2+}, Ba^{2+}	$[Al(H_2O)_5(OH)]^{2+}$ (for example)	$[Al(H_2O)_6]^{3+}$ and hydrated transition metal cations (such as $[Fe(H_2O)_6]^{3+}$) NH_4^+

Basic cations are conjugate bases of acidic cations such as $[Al(H_2O)_6]^{3+}$
-Acidic cations are limited to metal cations with 2+ and 3+ charges and to ammonium ions (and organic derivatives)
-All metal cations (M) are hydrated in water (of the form $[M(H_2O)_6]^{n+}$]. However, only when M is a 2+ or 3+ ion, and particularly a transition metal ion, does the ion act as an acid.



Logarithmic Scale and Relative Acid Strength

The $pK_a = -\log K_a$

Commonly used to compare relative acid strength

As pK_a decreases, acid strength increases

We'll see this again in chapter 18 with the Henderson-Hasselbalch equation.

Exercise 17.6

For each of the following salts in water, predict whether the pH will be greater than, less than, or equal to 7.

a) KBr b) NH_4NO_3 c) $AlCl_3$ d) Na_2HPO_4

Exercise 17.7

a) What is the pK_a value for benzoic acid, $C_6H_5CO_2H$ ($K_a = 6.3\times10^{-5}$)?

b) Is chloroacetic acid ($ClCH_2CO_2H$), $pK_a = 2.87$, a stronger or weaker acid than benzoic acid?

c) What is the pK_a for the conjugate acid of ammonia ($K_b = 1.8\times10^{-5}$)? Is this acid stronger or weaker than acetic acid ($K_a = 1.8\times10^{-5}$)?

Exercise 17.8

K_a for lactic acid, $CH_3CHOHCO_2H$, is 1.4×10^{-4}. What is K_b for the conjugate base of this acid, $CH_3CHOHCO_2^-$? Where does this base fit in table 17.3?

Answers:

17.6

a. KBr = **neutral** (both ions are from a strong acid and base)

b. NH_4NO_3 = **acidic** (ammonium is the conj. Acid of a weak base)

c) $AlCl_3$ = **acidic** (The Al^{3+} will act as a Lewis acid)

d) Na_2HPO_4 = **basic** (the hydrogen phosphate ion is the conjugate of the weak acid dihydrogen phosphate.

17.7

a. –log (6.3×10^{-5}) = **4.20**

b. **Stronger** (pK_a is smaller)

c. –log($1.0 \times 10^{-14}/1.8 \times 10^{-5}$) = **9.26** ($NH_4^+$)
Weaker. Acetic acid pKa = 4.74

17.8

K_b = ($1.0 \times 10^{-14}/1.4 \times 10^{-4}$) = **$7.1 \times 10^{-11}$**

It falls between formate (5.6×10^{-11}) and benzoate (1.6×10^{-10})

Example:

Determine the pH of a .050M solution of acetic acid (K_a = 1.8×10^{-5})

Determine the percent ionization of acetic acid for this solution.

Example:

A weak, monoprotic acid is found to ionize by 8.0% in a .020M solution. Determine the K_a value for the acid.

Answers:

1.* $$1.8 \times 10^{-5} = \frac{[H^+][A^-]}{[HA]} = \frac{[X][X]}{[.050 - X]}$$

$$X = .00094$$

$$-\log(.00094) = 3.027 \approx 3.0$$

% ionization = .00094/.050 = .0188 = 1.9%

2. 8.0% ionization in .020M
.080(.020M) = .0016M

$$K_a = \frac{(X)(X)}{(NM - X)} = \frac{(.0016)^2}{(.020 - .0016)} = 1.34 \times 10^{-4}$$

*Solve function on TI-89
Solve(1.8E-5=x∧2/(.050-x),x)

Example:

Calculate the difference in percent ionization for a .200M vs a 2.00×10^{-3}M formic acid ($HCHO_2$) solution. The K_a for formic acid is 1.9×10^{-4}.

Answer:
1.9×10^{-4} = (x)(x)/(.200-x)
x = .00607

% ionization = .00607/.200 = .03035 = 3.0%

1.9×10^{-4} = (x)(x)/(.00200-x)
x = .000529

% ionization = .000529/.00200 = .2645 = 26%

There is a 23% difference, with the greater ionization in the more dilute solution.

Approximating Equilibrium Calculation

Given: $$K_a = \frac{x^2}{a - x}$$

If $$\frac{x}{a} \leq 0.05$$

Then $$a - x \approx a$$

$$K_a = \frac{x^2}{a}$$

Do the approximation and see if x/a≤5%. Handy for "quick" calculations of equilibrium.

Ionization, pH and Polyprotic Acids

Polyprotic acids have more than one "proton" that can be released (e.g. H_2SO_4, H_3PO_4, H_2SO_3, etc.)

Primary, secondary and tertiary ionizations do not have the same K_a values

K_a values decrease with additional ionizations

Example:

Calculate the pH of a 5.00×10^{-1}M carbonic acid (H_2CO_3) solution. K_{a1}=4.4×10^{-7}; K_{a2}=4.7×10^{-11}

Answer:

1st Dissociation:
$H_2CO_{3(aq)} \leftrightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)}$ K_{a1}=4.4x10^{-7}
2nd Dissociation:
$HCO_3^-{}_{(aq)} \leftrightarrow H^+_{(aq)} + CO_3^{2-}{}_{(aq)}$ K_{a2}=4.7x10^{-11}
Note that each step produces H^+ ions

Step1:
$$4.4\times10^{-7} = \frac{(x)(x)}{(.500 - x)}$$
$$x = 4.69\times10^{-4}$$

Step2:
$$4.7\times10^{-11} = \frac{(.000469 + y)(y)}{(.000469 - y)}$$
$$y \approx 4.7\times10^{-11}$$

Clearly, the first dissociation dominates: 4.69x10^{-4} + 4.7x10^{-11} ≅ 4.69x10^{-4}. The final pH is –log(4.69x10^{-4}) = 3.3

Acidic and Basic Anhydrides

Substances that react with water to produce an acid or a base. Anhydride literally means "without water"

Acidic anhydride: Nonmetal oxide that in water forms an acid

$SO_3 + H_2O \rightarrow H_2SO_4$

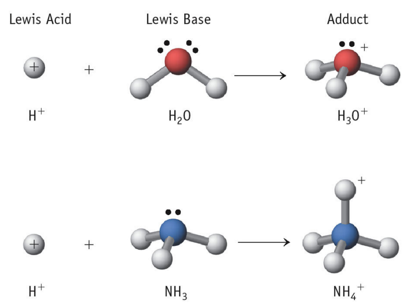
Basic anhydride: Metal oxide that in water forms a base

$Na_2O + H_2O \rightarrow 2NaOH$

Lewis Acids and Bases

Lewis Acid: Electron pair acceptor

Lewis Base: Electron pair donor



Cationic Lewis Acids:

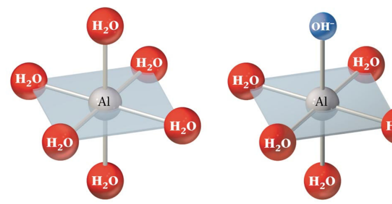
Hydrated Metal Cations (form coordinate covelent bonds)

Ex. $Al^{3+}{}_{(aq)} + 6H_2O_{(l)} \rightarrow [Al(H_2O)_6]^{3+}{}_{(aq)}$

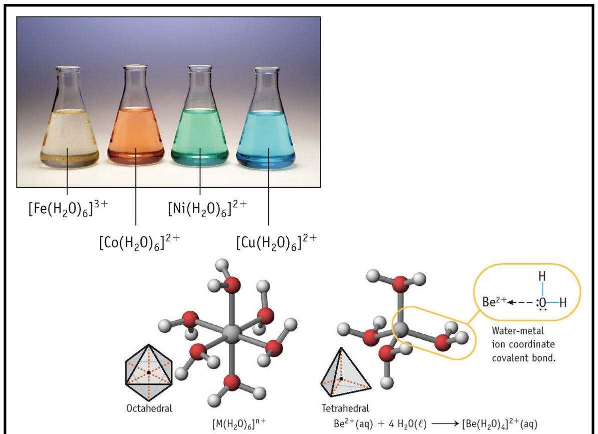
Known as "complex ions" (coordination complexes)

Many are very colorful

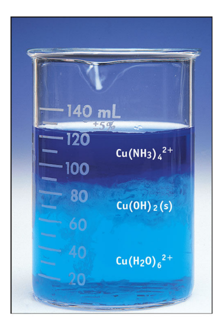
Acid form



Base form



Ammonia added to aqueous cupric sulfate.



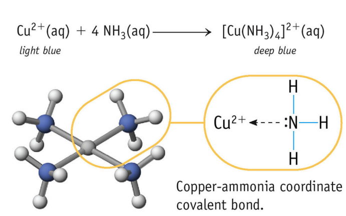
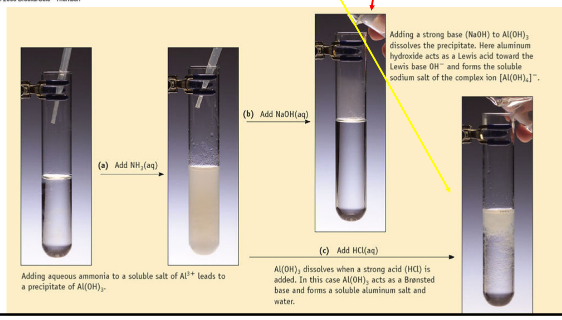


Table 17.6 Some Common Amphoteric Metal Hydroxides*

Hydroxide	Reaction as a Base	Reaction as an Acid
$Al(OH)_3$	$Al(OH)_3(s) + 3\ H_3O^+(aq) \rightleftharpoons Al^{3+}(aq) + 6\ H_2O(\ell)$	$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons [Al(OH)_4]^-(aq)$
$Zn(OH)_2$	$Zn(OH)_2(s) + 2\ H_3O^+(aq) \rightleftharpoons Zn^{2+}(aq) + 4\ H_2O(\ell)$	$Zn(OH)_2(s) + 2\ OH^-(aq) \rightleftharpoons [Zn(OH)_4]^{2-}(aq)$
$Sn(OH)_4$	$Sn(OH)_4(s) + 4\ H_3O^+(aq) \rightleftharpoons Sn^{4+}(aq) + 8\ H_2O(\ell)$	$Sn(OH)_4(s) + 2\ OH^-(aq) \rightleftharpoons [Sn(OH)_6]^{2-}(aq)$
$Cr(OH)_3$	$Cr(OH)_3(s) + 3\ H_3O^+(aq) \rightleftharpoons Cr^{3+}(aq) + 6\ H_2O(\ell)$	$Cr(OH)_3(s) + OH^-(aq) \rightleftharpoons [Cr(OH)_4]^-(aq)$



Molecular Lewis Acids

Oxides of nonmetals commonly act as Lewis acids

The attachment of oxygen to the less electronegative central atoms, draws electrons away from the central atom that is then attracted to the oxygen on the OH^- group.

Ex.

$CO_{2(g)} + OH^-_{(aq)} \rightarrow HCO_3^-{}_{(aq)}$

$SO_{2(g)} + OH^-_{(aq)} \rightarrow HSO_3^-{}_{(aq)}$

Molecular Structure, Bonding and Acid-Base Behavior

Behavior	Rationale	Example(s)
Hydrogen halide acid strength increases down the column	Electron affinity of halogen, Energy of solvation of acid and anion, **H-X bond energy** (decreases down)	HF<<HCl<HBr<HI (acid strength)
Oxoacid strength increases with attached oxygens	Additional oxygens increase the polarity of the O-H bond (inductive effect)[1]	HOCl<HOClO <$HOClO_2$<$HOClO_3$
Carboxylic acid strength increases with substituents with greater electronegativity	Greater electronegativity increases the polarization of the O-H bond	CH_3COOH< $CH_2ClCOOH$< $CHCl_2COOH$

1. Also stabilizes the anion (particularly with resonance)

Hydrated Metal Cations as Bronsted Acids

Small size and positive charge of the hydrated metal cation increases the polarization of the O-H bond on the water molecule (inductive effect) and the H^+ is released. 3+ ions tend to have greater acidity than 2+ ions.

Anions as Bronsted Bases

Anions (particularly oxoanions) tend to act as Bronsted bases attracting the H^+ from H_2O. Basicity of anion *increases with negative charge for related ions*. (Increase in basicity: $H_2PO_4^-$ <HPO_4^{2-}<PO_4^{3-})

Organic Amines as Bronsted/Lewis Bases

Contain derivative of ammonia (NH_3)
Nonbonding electron pair on nitrogen can act as an electron pair donor (proton acceptor)

Periodic Trends

1. Going across a row of elements of the periodic table. The electronegativity increases, the H-X bond polarity increases, and the acid strength increases. Strength increases down a group.

2. For a series of oxoacids of the same structure, differing only in the atom Y, the acid strength increases with the electronegativity of Y

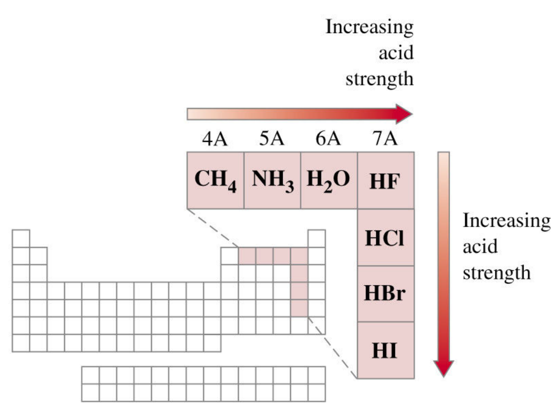
HIO < HBrO < HClO

3. For a series of oxoacids, $(OH)_mYO_n$, (e.g. H-O-Cl-O) the acid strength increases with n, the number of O atoms bonded to Y (excluding O atoms in OH groups).

HOCl < $HClO_2$ < $HClO_3$ < $HClO_4$

4. The acid strength of a polyprotic acid and its anions decreases with increasing negative charge (increased attraction to protons from negative charge)

HSO_4^- < H_2SO_4



Summary Question:17.119 (p847)

Consider a salt of a weak base and a weak acid such as ammonium cyanide. Both the NH_4^+ and CN^- ions interact with water in aqueous solution, but the net reaction can be considered as a proton transfer from NH_4^+ to CN^-

$NH_4^+{}_{(aq)} + CN^-{}_{(aq)} \leftrightarrow NH_{3(aq)} + HCN_{(aq)}$

a) Show that the equilibrium constant for this reaction, K_{net}, is $K_{net} = K_w / K_aK_b$, where K_a is the ionization constant for the weak acid HCN and K_b is the constant for the weak base NH_3.
b) Prove that the hydronium ion concentration in this solution must be given by $[H_3O^+] = (K_wK_a/K_b)^{1/2}$
c) What is the pH of a 0.15M solution of ammonium cyanide?

(a)

	$NH_4^+(aq) + H_2O(\ell) \leftrightarrow NH_3(aq) + H_3O^+(aq)$	$K_1 = K_w/K_b$
	$CN^-(aq) + H_2O(\ell) \leftrightarrow HCN(aq) + OH^-(aq)$	$K_2 = K_w/K_a$
	$H_3O^+(aq) + OH^-(aq) \leftrightarrow 2\ H_2O(\ell)$	$K_3 = 1/K_w$
	$NH_4^+(aq) + CN^-(aq) \leftrightarrow NH_3(aq) + HCN(aq)$	$K_{net} = K_1K_2K_3 = \dfrac{K_w}{K_aK_b}$

(b) From the ionization of the ammonium ion we can write the equation

$$[H_3O^+] = \frac{K_a[NH_4^+]}{[NH_3]} = \frac{\frac{K_w}{K_b}[NH_4^+]}{[NH_3]}$$

From the ionization of HCN we can write the equation $[H_3O^+] = \dfrac{K_a[HCN]}{[CN^-]}$

Combine these two equations into an expression for $[H_3O^+]^2$:

$$[H_3O^+]^2 = \frac{\frac{K_w}{K_b}[NH_4^+]}{[NH_3]} \cdot \frac{K_a[HCN]}{[CN^-]}$$

In any solution of NH_4CN, $[NH_4^+] = [CN^-]$ and $[HCN] = [NH_3]$. The equation for $[H_3O^+]^2$ can be simplified to

$$[H_3O^+]^2 = \frac{K_wK_a}{K_b} \text{ and } [H_3O^+] = \sqrt{\frac{K_wK_a}{K_b}}$$

(c) $$[H_3O^+] = \sqrt{\frac{K_wK_a}{K_b}} = \sqrt{\frac{(1.0\times10^{-14})(4.0\times10^{-10})}{1.8\times10^{-5}}} = 4.7\times10^{-10}\ M$$

$pH = -\log[H_3O^+] = 9.33$