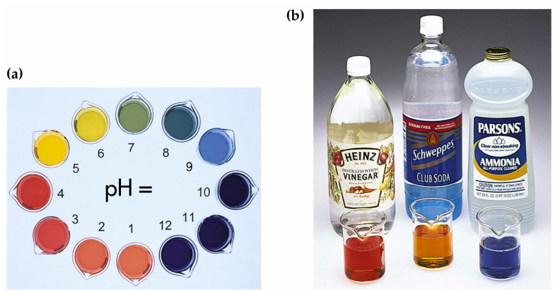
Acid – Base Chemistry



General Properties of Acids and Bases

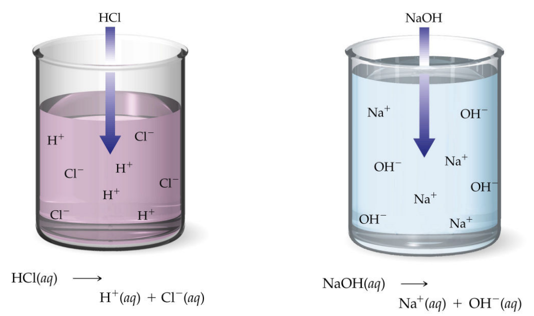
Acids:

- Turn litmus paper from blue to red
- React with active metals (e.g. $2HCl + Mg \rightarrow MgCl_2 + H_2$)
- Taste Sour
- React with bases to form water and salt

Bases:

- Turn litmus paper from red to blue
- Feel slippery or soapy on the skin
- Taste bitter
- React with acids to form water and salts.

Arrhenius Definition of Acids and Bases



Acids produce H^+ ions in solution

Bases produce OH^- ions in solution

Bronsted-Lowry Definition of Acids and Bases

Acid: Proton (hydrogen ion) donor

Base: Proton acceptor

Broadens definition of acids and bases

Water acting as a base

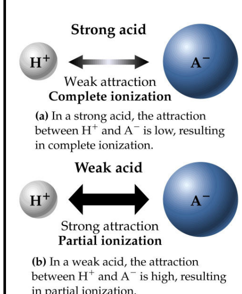
$$\underset{\text{Acid (Proton donor)}}{HCl(aq)} + \underset{\text{Base (Proton acceptor)}}{H_2O(l)} \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

Water acting as an acid

$$\underset{\text{Base (Proton acceptor)}}{NH_3(aq)} + \underset{\text{Acid (Proton donor)}}{H_2O(l)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

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.

Water is both amphoteric and amphiprotic



Usually H^+ and H_3O^+ (hydronium) refer to the same thing. The hydronium form shows the hydrogen ion's association with the water molecule in the solution.

The strength of an acid or base is dependent upon its ability to dissociate (or hydrolyze).

Strong vs. weak (based on the ability of the substance to dissociate (or hydrolyze))

Concentrated vs. dilute (based on the concentration (e.g. molarity) of the solute in solution.

Common Strong Acids

HCl, HBr, HI, H_2SO_4, HNO_3, $HClO_4$

Common Strong Bases

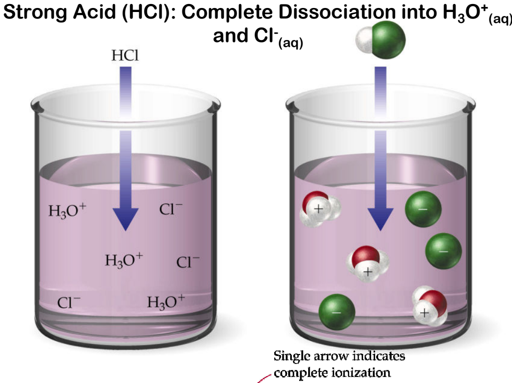
LiOH, NaOH, KOH, RbOH, CsOH

$Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$

Note: Although the last 3 are considered strong bases, their solubility is actually limited)

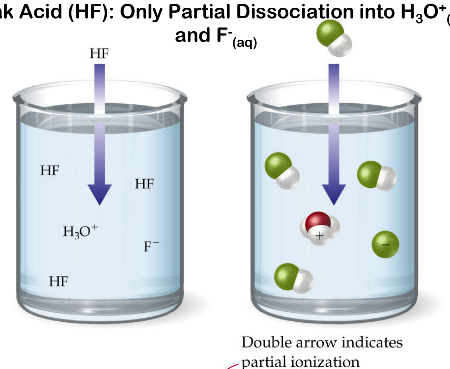
You should also know the weak base, ammonia (NH_3) and the weak acid, acetic acid (CH_3COOH).

Strong Acid (HCl): Complete Dissociation into $H_3O^+_{(aq)}$ and $Cl^-_{(aq)}$



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

Weak Acid (HF): Only Partial Dissociation into $H_3O^+_{(aq)}$ and $F^-_{(aq)}$



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

Conjugate Acid-base Pairs (From Bronsted-Lowry)

In an acid/base reaction, the acid identified on the reactant side becomes the conjugate base on the product side (because it would be the proton acceptor in the reverse direction). The converse is true for bases.

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

Base | Acid | Conjugate acid | Conjugate base

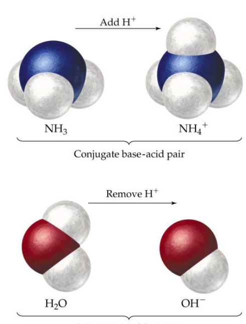
$$H_2SO_4(aq) + H_2O(l) \longrightarrow HSO_4^-(aq) + H_3O^+(aq)$$

Acid | Base | Conjugate base | Conjugate acid

Note: The stronger the acid or base is, the weaker its conjugate is.

Chemical equilibrium lies on the side of the stronger of the two counterparts.

Essentially conjugates differ by one proton (hydrogen ion).



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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

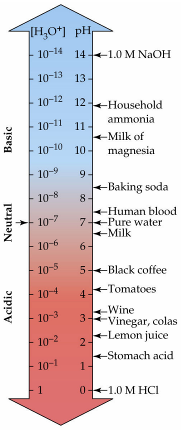
$pH = -\log[H^+]$ $\quad$ $[H^+] = 10^{-pH}$

$pOH = -\log[OH^-]$ $\quad$ $[OH^-] = 10^{-pOH}$

Ex. Calculate the pH of a .003M nitric acid solution.

Answer: Given $HNO_3 \rightarrow H^+_{(aq)} + NO_3^-{}_{(aq)}$

pH = -log (.003) = 2.52



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

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^- (in pure water) at any given time is 1.0×10^{-7}M

The product of the concentrations is given by:

$[H_3O^+][OH^-] = [1.0 \times 10^{-7}][1.0 \times 10^{-7}] = 1.0 \times 10^{-14} = K_w$

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 1.0×10^{-7} will have a pH less than 7 (given pH = $-\log[H_3O^+]$) and be acidic

Concentrations of H_3O^+ less than 1.0×10^{-7} will have a pH greater than 7 and be basic (alkaline)

Mathematical Implications:

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

$$pH + pOH = 14$$

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

Sample Questions:

1. Calculate the pH of a solution formed from adding 10.0g of NaOH into enough water to produce 1500mL of solution.

What is the hydroxide ion concentration of the solution?

2. Calculate the molarity of a nitric acid solution with a pOH of 8.3.

Answers:

1. $[OH^-]$ = (10.0g / 40.0g/mol) / 1.500L = .167M (hydroxide ion concentration)
pOH = -log .167 = .778 pH = 14.0 - .778 = 13.2

2. pH = 14.0 – pOH = 14.0 – 8.3 = 5.7
$[H_3O^+] = 10^{-pH} = 10^{-5.7} = 2.0 \times 10^{-6}M = [HNO_3]$

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 13.2, page 359 for K_a and K_b values

Table 17.3 Ionization Constants for Some Acids and Their Conjugate Bases at 25 °C

Acid Name	Acid	K_a	Base	K_b	Base Name
Perchloric acid	$HClO_4$	large	ClO_4^-	very small	perchlorate ion
Sulfuric acid	H_2SO_4	large	HSO_4^-	very small	hydrogen sulfate ion
Hydrochloric acid	HCl	large	Cl^-	very small	chloride ion
Nitric acid	HNO_3	large	NO_3^-	very small	nitrate ion
Hydronium ion	H_3O^+	1.0	H_2O	1.0×10^{-14}	water
Sulfurous acid	H_2SO_3	1.2×10^{-2}	HSO_3^-	8.3×10^{-13}	hydrogen sulfite ion
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	SO_4^{2-}	8.3×10^{-13}	sulfate ion
Phosphoric acid	H_3PO_4	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}	dihydrogen phosphate ion
Hexaaquairon(III) ion	$[Fe(H_2O)_6]^{3+}$	6.3×10^{-3}	$[Fe(H_2O)_5OH]^{2+}$	1.6×10^{-12}	pentaaquahydroxoiron(III) ion
Hydrofluoric acid	HF	7.2×10^{-4}	F^-	1.4×10^{-11}	fluoride ion
Nitrous acid	HNO_2	4.5×10^{-4}	NO_2^-	2.2×10^{-11}	nitrite ion
Formic acid	HCO_2H	1.8×10^{-4}	HCO_2^-	5.6×10^{-11}	formate ion
Benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	$C_6H_5CO_2^-$	1.6×10^{-10}	benzoate ion
Acetic acid	CH_3CO_2H	1.8×10^{-5}	$CH_3CO_2^-$	5.6×10^{-10}	acetate ion
Propanoic acid	$CH_3CH_2CO_2H$	1.3×10^{-5}	$CH_3CH_2CO_2^-$	7.7×10^{-10}	propanoate ion
Hexaaquaaluminum ion	$[Al(H_2O)_6]^{3+}$	7.9×10^{-6}	$[Al(H_2O)_5OH]^{2+}$	1.3×10^{-9}	pentaaquahydroxoaluminum ion
Carbonic acid	H_2CO_3	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}	hydrogen carbonate ion
Hexaaquacopper(II) ion	$[Cu(H_2O)_6]^{2+}$	1.6×10^{-7}	$[Cu(H_2O)_5OH]^+$	6.3×10^{-8}	pentaaquahydroxocopper(II) ion
Hydrogen sulfide	H_2S	1×10^{-7}	HS^-	1×10^{-7}	hydrogen sulfide ion
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}	hydrogen phosphate ion

Increasing Acid Strength ↑ / Increasing Base Strength ↓

Note that $K_aK_b=K_w$ for conjugate acid-base pairs

Weak Acids and Bases

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 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

An acid (or base) strength can also be expressed in terms of percent ionization:

$$\%ionization = \frac{[H^+]_{eq}}{[HB]_o} \times 100\%$$

(The percent ionization of the acid or base is inversely related to its molar concentration)

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

$$X = .00094$$

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

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

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

$$K_a = \frac{(X)(X)}{(NM - X)} = \frac{(.0016)^2}{(.020 - .0016)} = 1.39 \times 10^{-4}$$

*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 $$\frac{x}{a} \le 0.05$$

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 5.00x10^{-1}M carbonic acid (H_2CO_3) solution. K_{a1}=4.4x10^{-7}; K_{a2}=4.7x10^{-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

$Na_2O + H_2O \rightarrow 2NaOH$

Salt Solutions and pH

Recall, salts form from acid-base neutralization reactions:
Acid + Base → Salt + water

Salts in solution can affect the pH

For the soluble ions in solution, consider whether or not they are likely to act as Bronsted acids or bases.

Do they have any "strength" as an acid or base with respect to their conjugates?

Ions from weak conjugate bases can act as acids in solution (e.g. NH_4^+ comes from the weak base NH_3)

Ions from weak conjugate acids can act as bases in solution (e.g. NO_2^- comes from the weak acid HNO_2)

Salt	Resulting pH
KCl	Neutral (7)
KNO_2	Basic (>7)
$NO_2^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow HNO_{2(aq)} + OH^-{}_{(aq)}$	
NH_4Cl	Acidic (<7)
$NH_4^+{}_{(aq)} + H_2O_{(l)} \leftrightarrow NH_{3(aq)} + H_3O^+{}_{(aq)}$	

If both ions from the salt are from weak acids and bases, then the individual K_a and K_b values must be considered.

Example: Determine if the salt $LiCH_3COO$ (lithium acetate) is acidic, basic or neutral in solution.

Answer:

Li^+ comes from LiOH, a strong base, so it has no tendency to react with water.

CH_3COO^- comes from HCH_3COO, a weak acid, so it will react with water to some degree

$CH_3COO^-_{(aq)} + H_2O_{(l)} \leftrightarrow HCH_3COO_{(aq)} + OH^-_{(aq)}$

The solution will be basic

Example:

35.5g of lithium cyanide, LiCN is used to make 650.mL of solution.

a. Determine if the salt solution will be acidic, basic or neutral.

b. If the solution is acidic or basic, write a chemical equation showing why this takes place

c. Determine the pH of the solution. (See table p359)

Example:

35.5g of lithium cyanide, LiCN is used to make 650.mL of solution.

a. Determine if the salt solution will be acidic, basic or neutral.

Lithium is from a strong base to no reaction with water is likely. The cyanide ion, CN-, is from the weak acid hydrocyanic acid, so it is likely to react with water to some degree. The solution will be basic.

b. If the solution is acidic or basic, write a chemical equation showing why this takes place

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

c. Determine the pH of the solution (see table p359).

(35.5g/32.96g/mol) / .650L = 1.657M
$1.7x10^{-5} = [HCN][OH^-]/[CN^-] = (x)(x)/(1.657-x)$
X= $5.29x10^{-3} = [OH^-]$ pOH=2.27 pH = 14.0-2.27 = 11.7

Extra sample problems:

1. Calculate the pOH of a .150M solution of hydrocyanic acid, HCN.

What is the percent ionization of the solution?

K_a values on page 359.

2. 50.0mL of a .325M nitrous acid stock solution is diluted to 250.mL. If the K_a for nitrous acid is $6.0x10^{-4}$, what is the final pH of the solution?

Answers:

$5.8x10^{-10} = x^2 / (.150-x)$ x = $9.0x10^{-6}$

$-log(9.0x10^{-6}) = 5.05 = pH$

pOH = 14.0-5.05 = 8.95 = 9.0

.0500L(.325M) = .01625mol HNO_2

M = .01625mol/.250L = .0650M

$6.0x10^{-4} = x^2 / (.065-x)$ x = .005952

pH = -log(.005952) = 2.22534 = 2.2