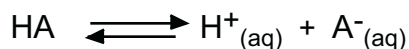


## Weak Acids

Weak acids do not dissociate completely in aqueous solutions.

They are somewhat stable molecules and therefore there is an equilibrium constant associated with their dissociation.

It's called the **acid dissociation constant,  $K_a$**



Again, this is just general notation for acids,  $\text{A}^-$  stands for the weak acid's anion

**Acid dissociation Constant.**  $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$   
( $K_a$  values are tabulated)

Here are some weak acids and their dissociation constants. Remember, for acids, if it is not a strong acid, it must be a weak acid. Memorize the strong ones—they are fewer in number.

<u>Weak Acid</u>	<u><math>K_a</math></u>	<u>Weak Acid</u>	<u><math>K_a</math></u>
Acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$	$1.8 \times 10^{-5}$	Hydrocyanic acid, $\text{HCN}$	$4.0 \times 10^{-10}$
Benzoic acid, $\text{HC}_7\text{H}_5\text{O}_2$	$6.6 \times 10^{-5}$	Hydrofluoric acid, $\text{HF}$	$6.7 \times 10^{-4}$
Chlorous acid, $\text{HClO}_2$	$1.1 \times 10^{-2}$	Hypobromous acid, $\text{HOBr}$	$2.1 \times 10^{-9}$
Cyanic acid, $\text{HOCN}$	$1.2 \times 10^{-4}$	Hypochlorous acid, $\text{HOCl}$	$3.2 \times 10^{-8}$
Formic acid, $\text{HCHO}_2$	$1.8 \times 10^{-4}$	Nitrous acid, $\text{HNO}_2$	$4.5 \times 10^{-4}$
Hydrazoic acid, $\text{HN}_3$	$1.9 \times 10^{-5}$	Sulfurous acid, $\text{H}_2\text{SO}_3$	$1.7 \times 10^{-2}$
Hydrogen sulfate ion, $\text{HSO}_4^-$	$1.0 \times 10^{-2}$	Carbonic acid, $\text{H}_2\text{CO}_3$	$4.4 \times 10^{-7}$
Propionic acid, $\text{HC}_3\text{H}_5\text{O}_2$	$1.4 \times 10^{-5}$	Dihydrogen phosphate ion, $\text{H}_2\text{PO}_4^-$	$6.2 \times 10^{-8}$
Hydrogen sulfide, $\text{H}_2\text{S}$	$1.0 \times 10^{-7}$	Ammonium ion, $\text{NH}_4^+$	$5.6 \times 10^{-10}$
Hydrogen sulfite ion, $\text{HSO}_3^-$	$6.0 \times 10^{-8}$	Hydrogen phosphate ion, $\text{HPO}_4^{2-}$	$4.5 \times 10^{-13}$
Hydrogen carbonate ion, $\text{HCO}_3^-$	$4.7 \times 10^{-11}$		

Okay, so dealing with weak acids is just like doing any equilibrium problem.

Set up the **ICE table**.

	$\text{HA}$	$\text{H}^+_{(\text{aq})}$	$\text{A}^-_{(\text{aq})}$
initial	$\frac{[\text{HA}]}{[\text{HA}]_0}$	--	--
change	$[\text{HA}]_0 - x$	$x$	$x$
equilibrium	$[\text{HA}]_0 - x$	$x$	$x$

This is assuming that we start by just dumping some HA into water

$$K_a = \frac{[x][x]}{[\text{HA}]_0 - x} = \frac{[x]^2}{[\text{HA}]_0 - x}$$

If, **If**,  $K_a < 10^{-5}$  or so, you may avoid the quadratic formula by assuming  $x$  will be much, much smaller than  $[\text{HA}]_0$  and just solving

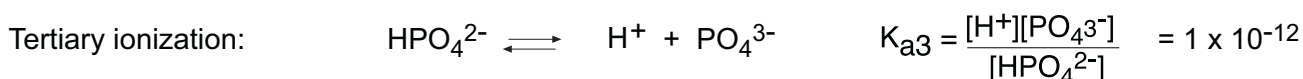
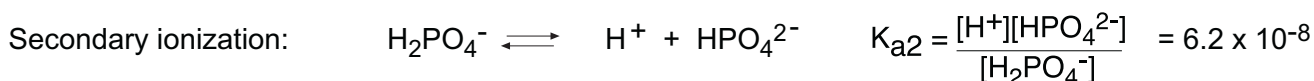
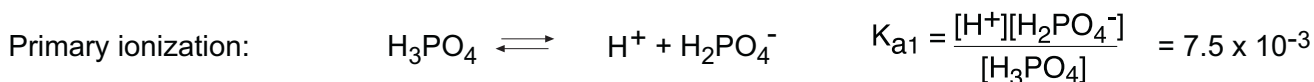
$$K_a = \frac{[x]^2}{[\text{HA}]_0}$$

Make sure  $K_a$  is small enough. You are expected to be able to use the quadratic equation

Or, just use your graphing calculator to solve the equation.

**Polyprotic Acids** <-- Now it's a tough call as to whether polyprotic acids are important enough for their own piece of paper. But you have to know how to deal with them, and it's a little confusing when you have something like  $\text{H}_3\text{PO}_4$  that has three dissociation reactions, each with their own  $K_a$ .

So this is what you've got going on:



**Step 1.** Look at the primary ionization, use an **ICE** table and figure out the concentration of species

$$K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{x^2}{[\text{H}_3\text{PO}_4]_0 - x} = 7.5 \times 10^{-3}$$

Use the quadratic equation to get x.  $x = [\text{H}^+] = [\text{H}_2\text{PO}_4^-]$

**Step 2.** Now use  $[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = x$  with the secondary ionization:

$$K_{a2} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \frac{x[\text{HPO}_4^{2-}]}{x} = 6.2 \times 10^{-8}$$

Solve for  $[\text{HPO}_4^{2-}]$  and

**LOOK!**

$[\text{HPO}_4^{2-}] = K_{a2}$  if  $\text{H}_3\text{PO}_4$  is the only source of hydrogen ions in the solution.

**Step 3.** Again, use the results of the previous steps calculations to do this one  $[\text{H}^+]$  from part 1 and  $[\text{HPO}_4^{2-}]$  from part 2. (I'll run this example assuming that  $[\text{HPO}_4^{2-}] = K_{a2}$ )

$$K_{a3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = \frac{x[\text{PO}_4^{3-}]}{K_{a2}} = 1 \times 10^{-12} = K_{a3}$$

And notice for this kind of a problem when you just dump  $\text{H}_3\text{PO}_4$  into water

$$[\text{PO}_4^{3-}] = \frac{K_{a3} K_{a2}}{x}$$

Standard weak acid problems you need to know how to solve

### 1. Given the pH of a weak acid solution, calculate the $K_a$ for the weak acid

Aspirin is a weak acid. A water solution is prepared by dissolving 0.1000 mol of aspirin (HAsp) per liter. The pH of the solution is 2.244. What is the  $K_a$  for Aspirin?

Set up the ICE table:

	$\text{HAsp}_{(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{Asp}^-_{(aq)}$		
Initial	0.1000	0	0
Change	$-5.702 \times 10^{-3}$	$5.702 \times 10^{-3}$	$5.702 \times 10^{-3}$
Equilibrium	$9.430 \times 10^{-3}$	$5.702 \times 10^{-3}$	$5.702 \times 10^{-3}$

There is no unknown. If you are given the pH, you are given the equilibrium concentrations of all species. You just need to do the arithmetic.

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-2.244}$$

$$[\text{H}^+] = 5.702 \times 10^{-3} \text{ M}$$

$$K_a = \frac{[\text{H}^+][\text{Asp}^-]}{[\text{HAsp}]} = \frac{(5.702 \times 10^{-3})(5.702 \times 10^{-3})}{(9.430 \times 10^{-3})} = 3.448 \times 10^{-4}$$

### 2. Sometimes "percent dissociation" is used to describe the acidity of a weak acid solution

$$\text{Percent dissociation of HA} = \frac{[\text{H}^+]}{[\text{HA}]_0} \times 100\%$$

Just as in the case when given the pH, percent dissociation is giving you the equilibrium concentrations of all species. You just need to do the arithmetic.

### 3. Given a weak acid, its $K_a$ and the concentration of a common ion, calculate equilibrium concentrations, pH and pOH

0.0250 moles of HCl and 0.100 moles of acetic acid are mixed in 0.365L of water.

Determine:  $[\text{CH}_3\text{COOH}]$ ,  $[\text{CH}_3\text{COO}^-]$ , pH and pOH.  $K_a = 1.8 \times 10^{-5}$

Set up the ICE table:

	$[\text{CH}_3\text{COOH}] \rightleftharpoons [\text{CH}_3\text{COO}^-] + [\text{H}^+]$		
Initial	0.274	0	0.0685
Change	-x	x	x
Equilibrium	$0.274 - x$	x	$0.0685 + x$

**Always use molar concentration in an ICE table**

$$[\text{CH}_3\text{COOH}]_0 = .100/.365 = .274 \text{ M}$$

$$[\text{H}^+]_0 = .0250/.365 = .0685 \text{ M}$$

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5} = \frac{(x)(.0685 + x)}{(0.274 - x)} \quad \text{SOLVE} \quad x = 5.99 \times 10^{-5} \text{ M}$$

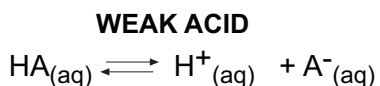
$$[\text{CH}_3\text{COOH}] = .274 \text{ M (3 sig figs)}$$

$$[\text{CH}_3\text{COO}^-] = 5.99 \times 10^{-5} \text{ M}$$

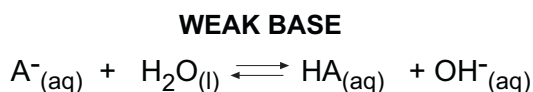
$$[\text{H}^+] = 5.99 \times 10^{-5} \text{ M and therefore pH} = -\log(5.99 \times 10^{-5}) = 4.22$$

$$\text{pOH} = 14 - \text{pH} = 9.78$$

### Acid dissociation constant and the dissociation constant for its conjugate base



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



$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

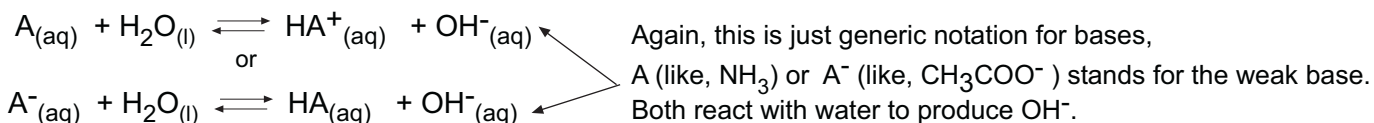
$$K_a K_b = \frac{[\text{H}^+][\text{A}^-][\text{HA}][\text{OH}^-]}{[\text{HA}][\text{A}^-]} = [\text{H}^+][\text{OH}^-] = K_w = 1 \times 10^{-14}$$

## Weak Bases

Weak bases do not dissociate completely in aqueous solutions.

They are somewhat stable molecules and therefore there is an equilibrium constant associated with their dissociation.

It's called the **base dissociation constant,  $K_b$**



I'm going to stick with the convention of  $A^-$  as the generic symbol for a weak base.

$$\text{Base dissociation Constant} \quad K_b = \frac{[HA][OH^-]}{[A^-]}$$

$K_b$  values are also tabulated but remember the relationship between the dissociation constants for a conjugate acid-base pair. You'll often be given  $K_a$  and have to calculate  $K_b$ .

$$K_a K_b = K_w = 1 \times 10^{-14}$$

Weak Base	$K_b$
Ammonia, $NH_3$	$1.8 \times 10^{-5}$
Aniline, $C_6H_5NH_2$	$4.6 \times 10^{-10}$
Hydrazine, $N_2H_4$	$9.8 \times 10^{-7}$
Methylamine, $CH_3NH_2$	$4.2 \times 10^{-4}$

\*By the way,  $K_a$  and  $K_b$  values vary and the values here may differ slightly from those in whatever text you are using.

**Use  $K_b$  to find  $[OH^-]$**  it's exactly the same equilibrium stuff, make the table, see what algebraic assumptions you can make etc.

	$A^-_{(aq)}$	$H_2O_{(l)}$	$HA^+_{(aq)}$	$OH^-_{(aq)}$
Initial	$[A^-]_0$	--	--	--
Change	$[A^-]_0 - x$		x	x
Equilibrium	$[A^-]_0 - x$		x	x

This is assuming that we start by just dumping a salt that contains  $A^-$  (the anion of a weak acid) into water

**Ex.** Calculate the pH of a 0.05 M  $CH_3COONa$  solution given the acid dissociation constant for acetic acid,  $K_a = 1.8 \times 10^{-5}$

Weak base =  $CH_3COO^-$  and  $K_b = K_w/K_a = 5.75 \times 10^{-10}$

	$CH_3COO^-_{(aq)}$	$H_2O_{(l)}$	$CH_3COOH_{(aq)}$	$OH^-_{(aq)}$
Initial	0.274		0	0
Change	-x		x	x
Equilibrium	0.274 - x		x	x

The chemistry here is that you've introduced the anion of a weak acid to solution, that's a weak base and you need to use the associated  $K_b$  to solve the Equilibrium problem.

$$K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]} = 5.75 \times 10^{-10} = \frac{(x)(x)}{(0.5 - x)} \quad \text{SOLVE} \quad x = 5.36 \times 10^{-6} \text{ M}$$

$$[OH^-] = 5.36 \times 10^{-6} \text{ M} \quad \text{and therefore } pOH = -\log(5.36 \times 10^{-6}) = 5.27$$

$$pH = 14 - pOH = 8.73$$

## Salt Solutions

Now there is another way that aqueous solutions can become acidic or basic.

By another way, I mean other than just dumping an acid or base into water.

It comes from the equilibrium of weak acids and weak bases.

## Basic Salts

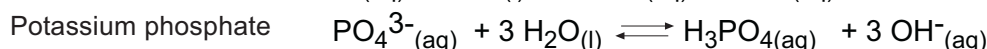
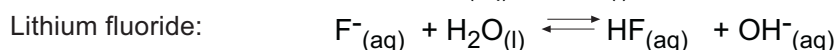
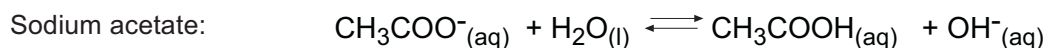
If you put a salt (ionically-bonded molecule) into water, the polar character of water will hydrate the individual ions, i.e. break up the molecule. In the case of an anion of a weak acid the ions will react with water to form the weak acid. And, the extent of this reaction is governed by the value of the corresponding  $K_a$ . Take a look:



When an anion of a weak acid reacts with water it forms the weak acid and hydroxide.

The solution therefore becomes basic and salts that contain the anions of weak acids are called basic salts. This makes sense because weak acid anions are in fact weak bases.

Here are some examples, all the salts are dumped into water:

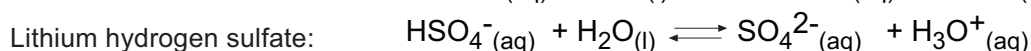
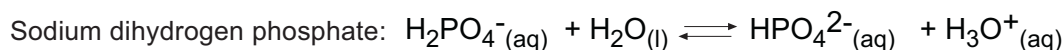


## Acidic Salts

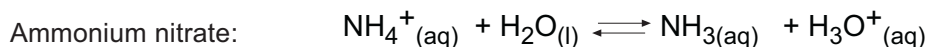
There are three different cases in which ions can form acidic solutions.

1. Some **amphoteric** (substance that can function as an acid or base) ions when put into water will dissociate to some small degree and the solution will become acidic. Typically the first anion of a polyprotic acid.

Here are some examples, again, all the salts are dumped into water:

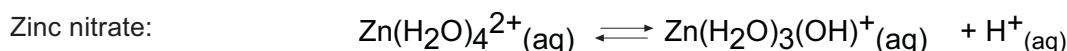


2. If you put an ammonium salt into water, the ammonium ion is a weak acid and the solution will become acidic.



3. The last case is also the typical example of a Lewis acid. If the cation of the salt is a transition metal, a complex ion can form and in this reaction the metal ion is acting as an electron pair acceptor—a Lewis acid.

Here is an example using hydrated zinc:



## Neutral Salts

There are a lot of salts that simply dissolve in water. The anions and cations of these salts are happy in their hydrated state and no chemical reaction occurs.

Neutral Salt Anions: Anions of strong monoprotic acids such as  $\text{Cl}^{-}$ ,  $\text{Br}^{-}$ ,  $\text{I}^{-}$ ,  $\text{NO}_3^{-}$ ,  $\text{ClO}_4^{-}$

Neutral Salt Cations: Group I metals and small Group II metals.