

**Chapter 15 Acids & Bases Summary**

Chemistry by Chang and Goldsby

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General Properties of Acids and Bases

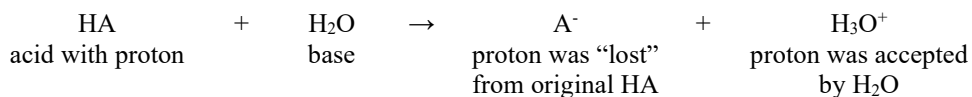
Brønsted Acids and Bases

Acid-Base Neutralization

This overview gives general information on acids and bases. After a quick read, you can go to Chapter 15.

**15.1 Brønsted Acid and Base Model**The Brønsted acid-base reaction model is centered on the transfer of a proton,  $H^+$ .

Acid-base properties are defined by an action and the ability to perform that action.

**An Acid is a proton donor.****A Base is a proton acceptor.**The reaction of HA acting as an acid and  $H_2O$  acting as a base:The two products,  $A^-$  and  $H_3O^+$ , are called conjugates.

The reactant acid becomes the conjugate base.

The reactant base becomes the conjugate acid.

The reacting acid or base and its conjugate are called the conjugate acid-base pair.

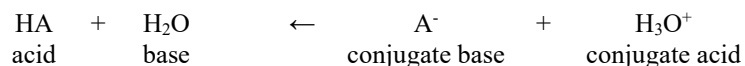
For the reaction:  $HA + H_2O \rightarrow A^- + H_3O^+$ 

conjugate acid-base pair	
HA Acid (reactant)	$A^-$ Conjugate Base (product)

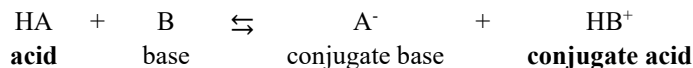
conjugate acid-base pair	
$H_2O$ Base (reactant)	$H_3O^+$ Conjugate Acid (product)

The reverse reaction is the reaction of the conjugates.

In the reverse reaction, the conjugate acid,  $\text{H}_3\text{O}^+$ , donates the proton to the conjugate base,  $\text{A}^-$ .  
In the reverse reaction, the conjugate base,  $\text{A}^-$ , accepts the proton from the conjugate acid,  $\text{H}_3\text{O}^+$ .



Any acid-base reaction is a competition between the forward action of the acid  $\rightarrow$  vs the  $\leftarrow$  reverse action of the conjugate acid.

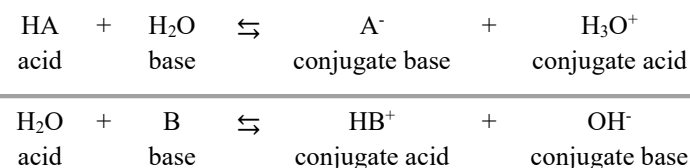


**Note!**

- (1) In all conjugate acid-base mixtures, the equilibrium concentrations of the **weaker acid will be present in higher concentrations**. The **equilibrium favors the weak** because the strong acid is better at donating its proton.
- (2) In all conjugate acid-base mixtures, the stronger base will always be on the same side as the stronger acid because it is better at accepting a proton.
- (3) The stronger the acid, the weaker its conjugate base.
- (4) The stronger the base, the weaker the conjugate acid.

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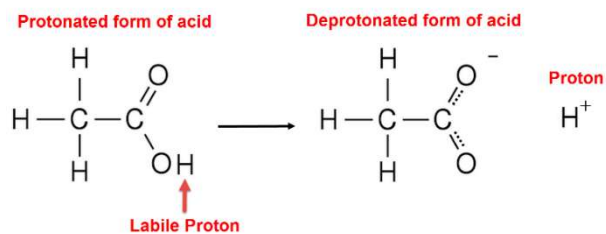
Some substances can both accept or donate protons depending on what they are reacting with. Such substances are called amphoteric. Water is an example of an amphoteric substance.



AP Chem terminology note:

In a molecule with numerous hydrogen atoms, only some of the H atoms may react as acids. The hydrogen atoms in a molecule that act as an acid are referred to as “labile protons”.<sup>1</sup>

As an example,  $\text{CH}_3\text{COOH}$ , ethanoic or acetic acid, has four hydrogen atoms, but of those four, only one is a labile proton. The other hydrogen atoms are too strongly bonded to the carbon atoms to act as an acid.



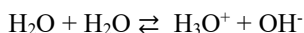

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<sup>1</sup> Most chemists see this as a misappropriation of the chemical term “labile”, but for purposes of the AP Chem exam we will use it with this meaning.

## 15.2 Acid-Base Properties of Water

The acid form of water can be written in two ways, as the hydronium ion,  $\text{H}_3\text{O}^+$ , or as a simple proton,  $\text{H}^+$ . The AP Chem equation sheet uses  $\text{H}_3\text{O}^+$ , but I prefer using  $\text{H}^+$  because it is easier to write. Both  $\text{H}_3\text{O}^+$  and  $\text{H}^+$  are used on the exam.

**Pure water and aqueous solutions always contain both  $\text{H}^+$  ( $\text{H}_3\text{O}^+$ ) and  $\text{OH}^-$  because water molecules react to form these two ions:**



**$\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are always present in water.**

Because  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are stronger Brønsted's they will be present in lower concentrations than  $\text{H}_2\text{O}$

Here are the two representations of water's autoionization reactions and the equilibrium expression.

$\text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$	$K_w = [\text{H}_3\text{O}^+] \times [\text{OH}^-]$
$\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq)$	or $K_w = [\text{H}^+] \times [\text{OH}^-]$

**You cannot change one of the product ion concentrations without affecting the other.**

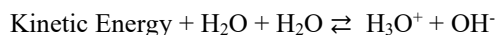
When outside sources introduce either  $\text{H}^+$  or the  $\text{OH}^-$  into an aqueous solution, water's own equilibrium will adjust the  $[\text{OH}^-]$  and  $[\text{H}_3\text{O}^+]$ .

**The product of the two ions' concentrations in water will always equal the  $K_w$ .**

**Important!** Neutral does not mean that  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are not present.

**Neutral water is defined when  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ .**

The autoionization of water is endothermic since the bond energy<sup>2</sup> of 2  $\text{H}_2\text{O}$  is greater than the bond energies of the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ . Questions on bond energy and this equilibrium are always asked on the exam.



lower potential energy  $\rightleftharpoons$  higher potential energy

stronger bonds  $\rightleftharpoons$  weaker bonds

$K_w$  increases with temperature as Le Châtlier's principle would predict from an endothermic reaction.

In a neutral solution,  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ , the concentrations of the ions change with temperature.

Temperature	neutral solution $[\text{H}_3\text{O}^+] = [\text{OH}^-]$	$K_w$ $[\text{H}_3\text{O}^+] \times [\text{OH}^-]$
0°C	$0.33 \times 10^{-7} M [\text{H}_3\text{O}^+] = 0.33 \times 10^{-7} M [\text{OH}^-]$	$0.1 \times 10^{-14}$
25°C	$1.0 \times 10^{-7} M [\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} M [\text{OH}^-]$	$1.0 \times 10^{-14}$
50.°C	$2.3 \times 10^{-7} M [\text{H}_3\text{O}^+] = 2.3 \times 10^{-7} M [\text{OH}^-]$	$5.5 \times 10^{-14}$
100.°C	$7.5 \times 10^{-7} M [\text{H}_3\text{O}^+] = 7.5 \times 10^{-7} M [\text{OH}^-]$	$56 \times 10^{-14}$

Neutral, hot water at 50°C has five times more “acid” and “base” than room temperature, neutral water.

<sup>2</sup>  $\Delta H_{rxn} = \Sigma \text{BE}_{\text{reactants}} - \Sigma \text{BE}_{\text{products}}$

The standard temperature for acid-base calculations is 25°C.

At 25°C the molar concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  will multiply to produce  $1.00 \times 10^{-14}$ .

Unless specifically told otherwise, you can assume the temperature of solutions will be at 25°C.

$$K_w = 1.00 \times 10^{-14} = [\text{H}^+] \times [\text{OH}^-] \text{ @ } 25^\circ\text{C} \quad \text{This is called the ion-product constant of water.}$$

$$\text{@ } 25^\circ\text{C} \quad \text{neutral water's } [\text{H}^+] = 1.0 \times 10^{-7} \text{ and } [\text{OH}^-] = 1.0 \times 10^{-7}$$

### 15.3 pH a Measure of Acidity in aqueous solutions

Acid and base concentrations routinely range from  $10^{-14} \text{ M}$  up to  $10^0 \text{ M}$ .

Converting concentrations into logarithms is a logical way of handling this wide range of numbers.

Most concentrations in acid-base calculations are less than  $1 \text{ M}$  resulting in log values that are negative.

To prevent always having negative values, the **p scale is defined as the negative of the logarithm.**

The negative log of acid-base numeric values results in positive p values that are typically 0 to 14.

Numbers	p values
$[\text{H}^+] = 10^{-\text{pH}}$	$\text{pH} = -\log[\text{H}^+]$
$[\text{OH}^-] = 10^{-\text{pOH}}$	$\text{pOH} = -\log[\text{OH}^-]$
$K = 10^{-\text{pK}}$	$\text{pK} = -\log[K]$

The use of logarithms allows the equilibrium expression to be changed into a simpler addition.

Acid Base Equilibrium Equation for all aqueous solutions	
using regular numbers	using -log values <sup>3</sup>
$K_w = [\text{H}^+] \times [\text{OH}^-]$	$\text{p}K_w = \text{pH} + \text{pOH}$
@ 25°C $1.00 \times 10^{-14} = [\text{H}^+] \times [\text{OH}^-]$	@ 25°C $14.00 = \text{pH} + \text{pOH}$

The first application of p values is with the autoionization of water.

For a neutral solution where  $[\text{H}^+] = [\text{OH}^-]$  at 25°C.

Numbers	-log values
$K_w = [\text{H}^+] \times [\text{OH}^-]$ $1.00 \times 10^{-14} = [1.00 \times 10^{-7}] [1.00 \times 10^{-7}]$	$\text{p}K_w = \text{pH} + \text{pOH}$ $14.00 = 7.00 + 7.00$

At 100.°C, an aqueous solution has a  $K_w = 5.6 \times 10^{-13}$  which translates to a  $\text{p}K_w = 12.26$ .

Therefore, at 100.°C, a neutral solution would have these concentrations and p values:

$$(7.5 \times 10^{-7} \text{ M } \text{H}^+) \times (7.5 \times 10^{-7} \text{ M } \text{OH}^-) = 5.6 \times 10^{-13}$$

$$6.13 \text{ pH} + 6.13 \text{ pOH} = 12.26 \text{ p}K_w$$

<sup>3</sup> Only the numbers to the right of the decimal place are significant in logarithm values. Show “p” answers to the hundredth’s place, but carry “p” calculations to the thousandth’s place to prevent rounding errors.

## 15.4 Strengths of Acids and Bases

### Strong Acids (the anions of strong acids are spectator ions<sup>4</sup>)

All strong acids are stronger than the conjugate acid of water,  $\text{H}_3\text{O}^+$ .

Therefore, all strong acids 100% change into  $\text{H}_3\text{O}^+(\text{aq})$  when dissolved in water.

AP Chemistry students are expected to know these six strong acids all of which are stronger than  $\text{H}_3\text{O}^+$ .

**The strong acids:**  $\text{HCl}$     $\text{HBr}$     $\text{HI}$     $\text{HNO}_3$     $\text{H}_2\text{SO}_4$     $\text{HClO}_4$

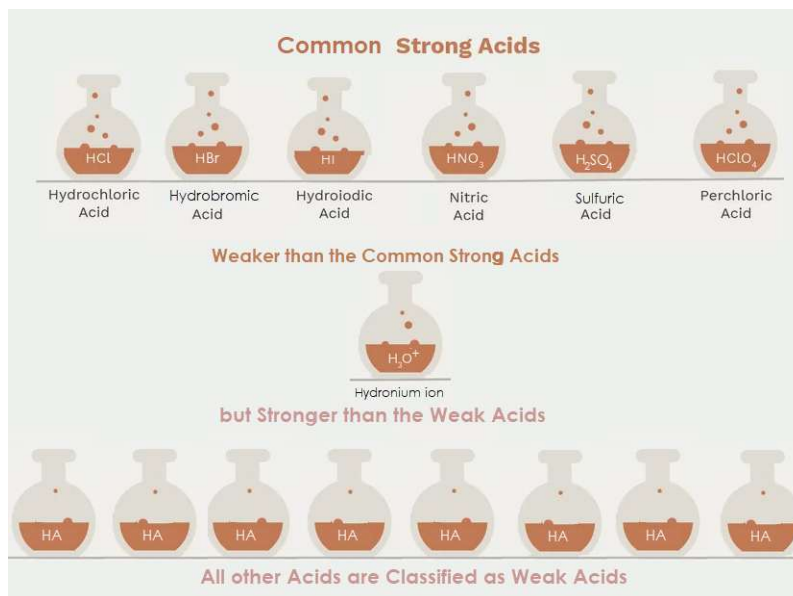
The strength of the six strong acids is so great that they ionize 100%.

No equilibrium expression needs to be used with strong acids.

**Just use simple stoichiometry when dealing with strong acid problems.**

**The reaction arrow for any strong acid reaction will be  $\rightarrow$ .**

Strong acid reactions in water are written as



The conjugate bases of five of the strong, monoprotic acids:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ , and  $\text{ClO}_4^-$  are all very stable and **are not considered to have any conjugate base properties in aqueous solutions.**

Therefore  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ , and  $\text{ClO}_4^-$  can be viewed as spectator ions in acid-base questions.

This will allow you to simplify problems by crossing them out and ignoring them in terms of pH or pOH.

<sup>4</sup> The exception to this statement is the conjugate base of  $\text{H}_2\text{SO}_4$ ,  $\text{HSO}_4^-$  which is a weak acid.

A 0.10 M strong acid would have this RICE chart:

Reaction	$\text{HA}_{\text{strong}}(aq)$	$\longrightarrow$ no significant equilibrium	$\text{H}^+(aq)$	+	$\text{A}^-(aq)$
Initial $M$	0.10		0		0
Change $M$	-0.10		+0.10		+0.10
Equilibrium $M$	$\approx 0.00$		0.10		0.10
pH			1.00		

**Bottom line:**  $[\text{H}^+] = [\text{HA}]_{\text{strong acids}}$       **pH =  $-\log[\text{HA}]_{\text{strong acids}}$**

All 0.1 M strong acid solutions:  $[\text{H}^+] = 0.1$  and  $\text{pH} = 1.0$

All 0.01 M strong acid solutions:  $[\text{H}^+] = 0.01$  and  $\text{pH} = 2.0$

Of note, while a strong acid solution with a pH of 2 will be caustic because of its low pH, **the solution could be easily neutralized since the solution contains only a small number of moles of acid.**

**Weak acids only partially ionize**, so the concentrations of the  $[\text{H}^+] < \text{HA}$  and equilibrium becomes significant requiring an equilibrium expression.

The anions (conjugate bases) of weak acids are not spectator ions and will act as conjugate bases, thus causing a Brønsted equilibrium. So you will need to use the equilibrium expression to work with weak acids.

The most common weak acids are organic carboxylic acids,  $-\text{COOH}$ .



Reaction	$\text{HA}(aq)$	$\rightleftharpoons$ equilibrium	$\text{H}^+(aq)$	+	$\text{A}^-(aq)$
Initial $M$	0.10		0		0
Change $M$	- small $x$		+ small $x$		+ small $x$
Equilibrium $M$	$0.10 - x \approx 0.10$		$x$		$x$
pH			$-\log[x]$		

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad K_a = \frac{[x][x]}{[0.10-x]} = \text{typically a small number less than } 1 \times 10^{-4}$$

Solving for  $x$ , the exact  $[\text{H}^+]$ , would involve a **quadratic equation which will never be required** on the AP Chem exam.

Instead, as explained later, the simplifying approximation that will allow for a quick determination of the  $[\text{H}^+]$  using the following equation which is not found on the AP Equations sheet.

**This equation will allow you to quickly solve weak acid problems.**

$$[\text{H}^+] \approx \sqrt{[\text{HA}_{\text{weak}}] \times K_a}$$

**You will use these equations on every AP Chemistry exam:**

**Strong Acids:**  $[H^+] = [HA_{\text{strong}}]$        $pH = -\log [HA_{\text{strong}}]$

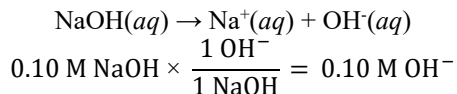
**Weak acids:**  $[H^+] \approx \sqrt{[HA_{\text{weak}}] \times K_a}$        $pH \approx -\log(\sqrt{[HA_{\text{weak}}] \times K_a})$

### Strong Bases pOH

The only strong base that you will need to deal with is the hydroxide ion,  $OH^-(aq)$ <sup>5</sup>.

Strong base problems will involve dissolving a soluble ionic hydroxide compound. (e.g. NaOH, KOH)

For example, you would be asked to find the pH of a 0.10 M NaOH(aq). Sodium hydroxide is soluble and would completely ionize to make hydroxide ions.



$$pOH = (-\log 0.10 \text{ M}) = 1.00$$

Solutions are best viewed in terms of  $[H^+]$ . So alkaline solutions require an extra calculation to find the  $[H^+]$  based on the  $[OH^-]$ .

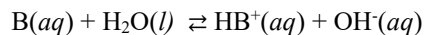
For example, the steps involved in finding the pH of a 0.10 M  $OH^-$  solution would require using the autoionization equilibrium of water.

This can be done two ways:

$K_w = 1.00 \times 10^{-14}$ $1.00 \times 10^{-14} = [H^+] \times [OH^-]$ $1.00 \times 10^{-14} = [H^+] \times [0.10]$ $[H^+] = 1.0 \times 10^{-13} \text{ M}$ $pH = 13.00$	$pK_w = 14.00$ $pK_w = pH + pOH$ $14.00 = pH + pOH$ $14.00 = pH + 1.00$ $pH = 13.00$
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<sup>5</sup> The hydride ion,  $H^-$ , is an even stronger base than  $OH^-$ , but it has never been used on the AP exam and are unlikely to be seen in any AP Chem exam. However, hydride chemistry has many important applications, and you should at least know it exists.

**Weak Bases like weak acids only partially ionize and have a complication because they react by accepting protons from water so the equilibrium equation must show  $\text{H}_2\text{O}(l)$ .** However, since the concentration of water doesn't significantly change, water is not included in the equilibrium expression.



$$\text{Weak bases } [\text{OH}^-] < [\text{B}]$$

Of note: Many weak bases are the conjugates of weak acids,  $\text{B}^-$ . So, you will be dealing with both B and  $\text{B}^-$  as base abbreviations.

The common weak bases are:

amines,  $\text{C-NH}_2$    ammonia,  $\text{NH}_3$    conjugate base anions of weak acids,  $\text{A}^-$

**Bottom line these equations are used with bases:**

**Strong bases,  $\text{OH}^-$ :**

$$[\text{B}_{\text{strong}}] = [\text{OH}^-]$$

$$\text{pOH} = -\log[\text{B}_{\text{strong}}]$$

$$\text{pH} = 14.00 - \text{pOH}$$

**Weak bases:**

$$\text{pOH} \quad [\text{OH}^-] \approx \sqrt{[\text{B}_{\text{weak}}] \times K_b} \quad \text{pOH} \approx -\log(\sqrt{[\text{B}_{\text{weak}}] \times K_b}) \quad \text{pH} = 14.00 - \text{pOH}$$

### 15.5 Weak Acids and Ionization Constants

Note: The molar concentration of an acid solution is  $[\text{HA}]$  is based on how the solution was initially made, that is, the moles of solute HA that were dissolved to make 1 liter of solution.

However, the HA immediately reacts with  $\text{H}_2\text{O}$ , to make an equilibrium mixture with  $\text{H}_3\text{O}^+$  and  $\text{A}^-$ .

Therefore, the  $[\text{HA}]_{\text{eq}}$  at equilibrium will be slightly less than given concentration of the solution,  $[\text{HA}]_{\text{initial}}$ .

The equilibrium  $[\text{H}_3\text{O}^+]$  determines the true acidity of the solution and the pH.

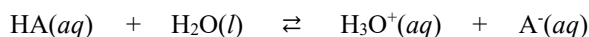
When a problem says that you have a 0.100 M solution of a weak acid, HA, that concentration is the initial concentration and is only valid for the initial row in a RICE table.

The equilibrium  $[\text{HA}]$  will be slightly less than the initial  $[\text{HA}]$ .

**Weak acid problems require the use of RICE tables and the equilibrium expression.**

Because a weak acid holds on to its proton more tightly, the forward reaction  $\rightarrow$  is not as strong, and you must deal with a true equilibrium  $\rightleftharpoons$ .

Therefore, the  $K_a$  and percent ionization of the weak acid comes into play.



An **important simplification** involving weak acids is that the initial  $[\text{HA}_{\text{weak}}]$  is usually not noticeably changed at equilibrium since the amount of the original acid that ionizes is small.



For example: HA is a weak acid with a  $K_a$  of  $7.1 \times 10^{-5}$ . What is the  $[H^+]$  and pH of a 0.10 M HA solution?

Reaction	Ha(aq)	$\rightleftharpoons$ equilibrium	H <sup>+</sup> (aq)	+	A <sup>-</sup> (aq)
Initial <i>M</i>	0.10		0		0
Change <i>M</i>	- <i>x</i>		+ <i>x</i>		+ <i>x</i>
Equilibrium <i>M</i>	0.10 - <i>x</i>		<i>x</i>		<i>x</i>
pH			-log[ <i>x</i> ]		

Using the equilibrium expression and  $K_a$ , you can solve for the  $[H^+]$  if you know how to solve polynomial expressions.

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad 7.1 \times 10^{-5} = \frac{[x][x]}{[0.10 - x]}$$

Solving for  $x$  in this weak acid problem requires a quadratic equation or a graphing calculator equation solver. However, AP Chemistry problems are set up so as not to require quadratic skills. All AP Chemistry “quadratic” problems can be solved with the use of approximation.

Here is how the approximation method can be used instead of the quadratic equation.

The amount of weak acid that is ionized,  $-x$ , will be small compared to the original concentration of the weak acid  $[HA]_{\text{Initial}}$ . Therefore  $[HA - x]_{\text{Equilibrium}} \approx [HA]_{\text{Initial}}$

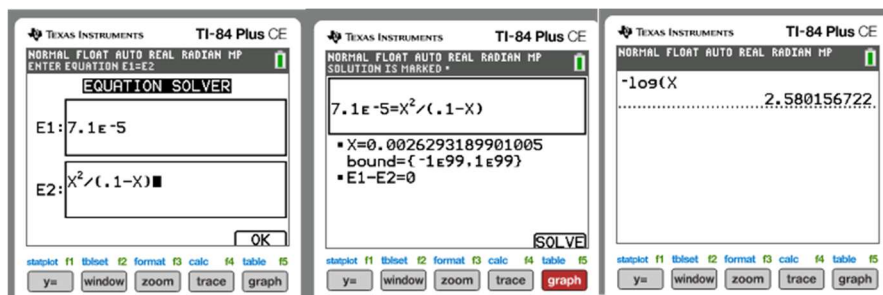
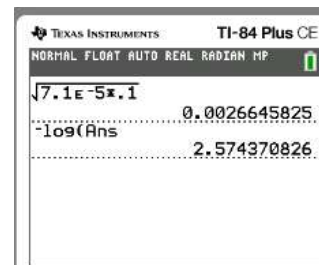
In the previous example if  $x$  is ignored in the denominator subtraction since  $0.10 - x \approx 0.10$

$$7.1 \times 10^{-5} = \frac{[x][x]}{[0.10 - x]} \quad 7.1 \times 10^{-5} \approx \frac{[x][x]}{[0.10]} \quad [x] \approx \sqrt{7.1 \times 10^{-5} \times 0.10} \quad [x] \approx 0.0027 M$$

$$[H^+] = 0.0027 M \quad pH = -\log[0.0027] \quad pH = 2.57$$

the final pH answer is close enough to be marked as correct.

This is how solving the problem without the  $-x$  simplification would be solved on a graphing calculator.



Since the College Board doesn't want to penalize students who do not have graphing calculators which can easily solve polynomial expressions, any weak acid problem which would require a quadratic equation for solutions on the exam will allow the use of approximation:

$$[H^+] \approx \sqrt{[HA_{\text{weak}}] \times K_a}$$

**For the third time, this probably the most important equation in weak acid chemistry.**

$$[H^+]_{\text{equilibrium}} \approx \sqrt{[HA_{\text{weak}}]_{\text{start}} \times K_a}$$

**Percent Ionization:**

Percent Ionization gives the extent of an acid's ability to produce  $[H^+]$  and is an indication of an acid's strength.

$[HA]_{\text{initial}}$  in the first row of the RICE chart is used in determining % Ionization

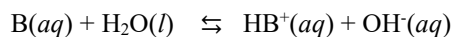
$\% \text{ Ionization} = \frac{[H^+]_{\text{equil}}}{[HA]_{\text{initial}}} \times 100$	<p>The % ionization uses the starting concentration of the weak acid <math>HA_{\text{initial}}</math>, rather than the equilibrium concentration of the remaining acid, <math>[HA]_{\text{eq}}</math>, in the Equilibrium row.</p> <p><b>The % ionization of strong acids is 100%.</b>  <b>The % ionization of weak acids is typically less than 5%.</b></p>
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%Ionization of acids and bases increases with dilution. However, the dilution factor still will decrease the acid or base concentration despite the increase in ionization. This is a common test question, so it is worth remembering.

$[HA]_{\text{start}}$	% Ionization	pH
1.00	1%	1.9
0.80	1%	1.9
0.60	2%	2.0
0.40	2%	2.1
0.20	3%	2.2
0.05	6%	2.5

## 15.6 Weak Bases and Base Ionization Constants

Weak bases react with water to form an equilibrium that produces the conjugate acid of the weak base and the hydroxide ion. While similar to weak acids, the equilibrium equation of a weak base is more complicated since you must include water in the reaction equation.



Weak bases follow the same percent ionization equation except with the hydroxide ion.

$$\% \text{ Ionization} = \frac{[OH^-]_{\text{equil}}}{[Base]_{\text{initial}}} \times 100$$

The equilibrium expression for the weak base equilibrium on the equation sheet.

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

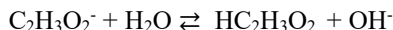
Notable weak bases: ammonia, amines, and the conjugate bases of weak acids.

Ammonia is the simplest of the molecular weak bases.

The reaction is written as  $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

However the weak conjugate bases of acids are anions and the charges will be different.

For example the conjugate base of acetic acid  $HC_2H_3O_2$  is the acetate ion  $C_2H_3O_2^-$  often written with its soluble cation, sodium acetate,  $NaC_2H_3O_2$ . When dissolved in water the ionization of the weak base is:



Weak base equations are like those used with weak acids.

The major difference is that the  $[OH^-]$  at equilibrium is found, and then from the  $[OH^-]$  the  $[H^+]$  is determined using the ionization of water equation.

$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$ $K_b = \frac{[OH^-][HB^+]}{[B]}$	<p>Just as in the case of weak acids, you can use the simplifying assumption to avoid having to use the quadratic equation to solve for the hydroxide ion concentration.</p>
<p>In most cases <math>[Base]_{\text{initial}} \approx [Base]_{\text{equilibrium}}</math></p> $[OH^-] \approx \sqrt{K_b \times [B]_{\text{initial}}}$ $[H^+] \approx \frac{1.00 \times 10^{-14}}{[OH^-]}$	<p>Since most questions ask for the concentration of the <math>[H^+]</math> in the resulting solution, there is the <b>extra step</b> of finding the depressed level of the <math>[H^+]</math> using the ion product equation of water.</p> $1.00 \times 10^{-14} = [H^+] \times [OH^-]$ <p>Alternately <math>14.00 = \text{pH} + \text{pOH}</math> can be used.</p>

Even though  $[\text{OH}^-] \approx \sqrt{K_b \times [\text{B}]_{\text{initial}}}$  is a fast method of solving weak base problems, it is wise to make a RICE chart to understand what is happening in a weak base problem.

For example, a weak base with a concentration of 0.10 M

Reaction	$\text{B (aq)} + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{HB}^+(\text{aq})$	+	$\text{OH}^-(\text{aq})$
Initial $M$	0.10		0		0
Change $M$	-very small $x$		$+x$		$+x$
Equilibrium $M$	$\approx 0.10$		$x$		$x$
			pOH		$-\log[x]$

Also, the weak base can be an anion of a weak Brønsted acid.

Reaction	$\text{B}^-(\text{aq}) + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{HB (aq)}$	+	$\text{OH}^-(\text{aq})$
Initial $M$	0.10		0		0
Change $M$	-very small $x$		$+x$		$+x$
Equilibrium $M$	$\approx 0.10$		$x$		$x$
			pOH		$-\log[x]$

$$K_b = \frac{[\text{OH}^-][\text{HB}^+]}{[\text{B}]} \text{ or } \frac{[\text{OH}^-][\text{HB}]}{[\text{B}^-]}$$

$$K_b \approx \frac{[x][x]}{[.10 - [x]]}$$

$$\text{pOH} = -\log(x)$$

$$\text{pH} = 14.00 - \text{pOH}$$

### 15.7 The Relationship Between the Ionization Constants of Acids and their Conjugate Bases.

Unlike strong acids, once a weak acid has reacted, its conjugate base becomes a significant player in solutions. This is because the conjugate base of a weak acid will react with water to produce a basic solution once the acid has been reacted.

To determine the conjugate base's effect on a solution, you must know its  $K_b$ .

If you know the  $K_a$  of an acid, you can quickly find the  $K_b$ .

$$K_w = 1.00 \times 10^{-14} = K_a \times K_b$$

$$\text{p}K_w = 14.00 = \text{p}K_a + \text{p}K_b$$

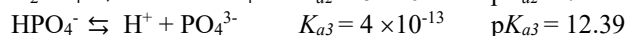
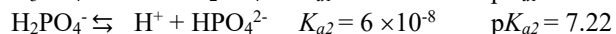
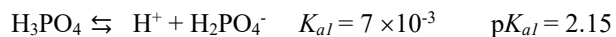
This will come into play in titrations and buffers.

## 15.8 Polyprotic Acids

A polyprotic acid can donate more than one proton.

The first proton of a polyprotic acid will be the easiest to ionize.

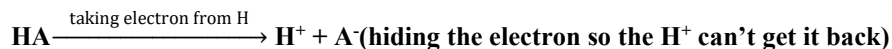
Subsequent protons may act as acids, but they will have smaller ionization constants.



Note: the larger the p value the smaller the  $K$

## 15.9 Molecular Structure and Strength of Acids

Acid strength is based on taking the electron from the labile hydrogen atom and hiding it.



The more electronegative A is, the more likely it will take the electron from the H

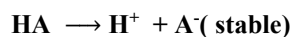
Oxygen atoms are very good at taking electrons from H so the more O atoms the stronger the acid.

<p><b>HClO</b> fewest oxygens</p> <p><b>WEAK</b></p>	<p><b>HClO<sub>4</sub></b> most oxygens</p> <p><b>STRONG</b></p>
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Other electronegative atoms can assist in taking the electron from H.

<p><b>HIO</b> I has a low electronegativity</p> <p><b>WEAK</b></p>	<p><b>HClO</b> Cl has a high electronegativity</p> <p><b>STRONG</b></p>
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The more stable  $\text{A}^-$  is the less likely  $\text{H}^+$  can regain its electron.



**Strong acids have weak, stable conjugate bases** (anions)

The rationale is that if the conjugate base is stable, the less likely it is for the conjugate base to act as a base by “rejoining” with the  $\text{H}^+$ .

Factors that make strong acids is that the stability of the conjugate base is enhanced by

- (1) Size, the greater the size of the conjugate base the more diffused its charge, so it will not attract  $\text{H}^+$ .
- (2) Resonance, if the anion has a structure with resonating bonds, it will be more stable.

### 15.10 Acid-Base Properties of Salt Solutions

Hydrolysis of ionic compounds (salts) is the reaction of an ionic compound with water to produce an acidic or alkaline solution.

To have a salt produce an acidic or basic solution it must contain an ion from a weak acid or weak base.

**To estimate the pH of a dissolved salt: mildly acidic, mildly alkaline, or neutral.**

To predict the acidity, alkalinity, or neutral characteristics of a soluble ionic compound.

- 1. Cross out any alkali metal ion or alkaline earth metal ion.**  
These cations will always be spectators in solutions.
- 2. Cross out any anion from the monoprotic strong acids** ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ).  
These anions will always be spectators in solutions.
- (a) Remaining uncrossed-out cations will make the solution mildly acidic.**
  - (b) Remaining uncrossed-out anions will make the solution mildly basic.**
  - (c) If both ions were crossed out, then the solution will be neutral.**

Determine the acid or base characteristics of these ionic compounds:



1. Crossing out the alkali metal or alkaline earth cations.

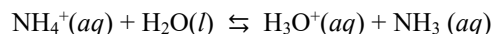


2. Crossing out any anion from the monoprotic strong acids

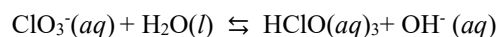


3. The remaining ions:  $\text{C}_2\text{H}_3\text{O}_2^-$   $\text{ClO}_3^-$   $\text{CO}_3^{2-}$   $\text{NH}_4^+$

The cation reacts with water to produce slightly acidic solutions.



The anions react with water to produce slightly alkaline solutions.



**Bottom line:**

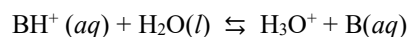
**Soluble salts made from the conjugate ions of weak acids will be mildly basic.**

**Soluble salts made from the conjugate ions of weak bases will be mildly acidic.**

**Ignore alkali metal ions, alkaline earth ions,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ , and  $\text{ClO}_4^-$  in any acid-base problems.**

**Acidic hydrolysis** uses the cation,  $\text{BH}^+$

The cations of ionic compounds conjugate of weak bases, such as  $\text{NH}_4\text{Cl}$ , act as a weak acid.



Steps to find the  $[\text{H}^+]$  of an ionic salt, that undergoes acid hydrolysis:

- (1) Determine the concentration of the cation,  $[\text{HB}^+]$
- (2) Find the  $K_a$  of the acid from its conjugate base, B,  $K_b$  which will be given in the problem.

$$1.00 \times 10^{-14} = K_a \times K_b$$

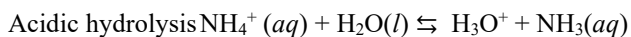
- (3) Ionic hydrolysis only produces very weak acid solutions and creating a RICE table is not necessary.

$$[\text{H}^+] = \sqrt{K_a \times [\text{HB}^+]}$$
 always works.

Example:

Calculate the pH of 0.200 M  $\text{NH}_4\text{Cl}$  solution. ( $K_b \text{ NH}_3 = 1.8 \times 10^{-5}$ )

With a 1:1 ratio 0.200 M  $\text{NH}_4\text{Cl}$ , = 0.200 M  $\text{NH}_4^+(aq)$  .



Find the  $K_a$  of this acid from the  $K_b$  of its conjugate base,  $\text{NH}_3$  which is given in the problem.

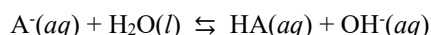
$$1.00 \times 10^{-14} = K_a \times K_b \quad 1.00 \times 10^{-14} = K_a \times 1.8 \times 10^{-5} \quad \text{NH}_4^+ \quad K_a = 5.6 \times 10^{-10}$$

In salt hydrolysis, you can always use the short cut equation for  $[\text{H}^+]$  of a weak acid.

$$[\text{H}^+] = \sqrt{K_a \times [\text{NH}_4^+]} \quad [\text{H}^+] = \sqrt{5.6 \times 10^{-10} \times [0.20]} \quad [\text{H}^+] = 1.1 \times 10^{-5}$$

$$-\log[1.1 \times 10^{-5}] = 4.98 \quad \text{pH} = 4.96 \text{ mildly acidic}$$

**Alkaline hydrolysis** uses an anion,  $\text{A}^-$ , the conjugate base of a weak acid, such as NaF



A quick solution method for hydrolysis with  $\text{A}^-$ .

- (1) Find the  $\text{A}^-$  concentration
- (2) Find the  $K_b$  of  $\text{A}^-$  using the  $K_a$  of the conjugate acid HA. ( $1.00 \times 10^{-14} = K_a \times K_b$ )
- (3)  $[\text{OH}^-] = \sqrt{K_b \times [\text{A}^-]}$  ...then go to find the pH

#### 15.11 Acid-Base Properties of Oxides... not in AP Chem

nonmetal oxides dissolve in water to make acids  
metal oxides dissolve in water to make bases

#### 15.12 Lewis Acids are not part of the AP Chemistry curriculum.