

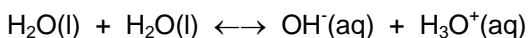
Acids and Bases

Know the definition of Arrhenius, Bronsted-Lowry, and Lewis acid and base.

Autoionization of Water

Since we will be dealing with aqueous acid and base solution, first we must examine the behavior of water.

- 1) In pure water, to which no electrolytes have been added, there is a small electrical conductivity, indicating that there are ions present. This is due to the **autoionization of water**.



OH^- is the hydroxide ion.

H_3O^+ is the hydronium ion

The hydronium ion represents a proton that is hydrated by (surrounded by) water. There is never "just a proton" in solution. However, the hydronium ion is often represented by "just a proton" and the autoionization is written as a dissociation reaction.



- 2) This equilibrium can be described by an equilibrium expression: $K_{\text{eq}} = [\text{H}^+][\text{OH}^-]$. This is given a special name and symbol. **K_w , the ion product of water**.

Experimentation shows that at a particular temperature, K_w is constant. At 25°C , $K_w = 1 \times 10^{-14}$. At 25° it will always be true that $1 \times 10^{-14} = [\text{H}^+][\text{OH}^-]$

- 3) If water is the only source of protons, then **$[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7}$** and the solution is considered **neutral**.
If **$[\text{H}^+] > [\text{OH}^-]$** , then the solution is **basic**.
If **$[\text{H}^+] < [\text{OH}^-]$** , then the solution is **acidic**.

Be able to write the equation for the autoionization of water.

If given $[\text{H}^+]$ be able to calculate $[\text{OH}^-]$ and vice versa.

The pH of aqueous solutions

- 1) Since the concentrations of $[\text{H}^+]$ and $[\text{OH}^-]$ observed are often very small, the p-scale is used to indicate the quantity present.

$$\text{p}(X) = -\log(X)$$

We use this to determine pH, the pOH, $\text{p}K_a$, and $\text{p}K_b$ values.

Note:

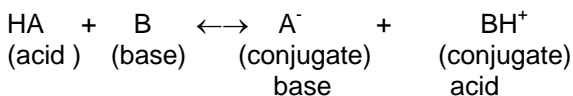
- 1) There is an inverse relationship. For example, as $[\text{H}^+]$ increase, the pH decreases.
 - 2) As the concentration changes by 10^n , the pH will change by n. For example if the concentration changes by a factor of 100 or 10^2 , the pH will change by 2.
- 2) Applying the p scale to the equation for autoionization of water:
 $K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$ results in $\text{p}K_w = \text{pH} + \text{pOH} = 14$

If given $[\text{H}^+]$ or $[\text{OH}^-]$ be able to calculate pH and pOH.

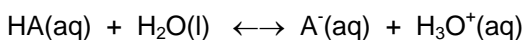
Behavior of Solutes in Water

When a solute is added to water, a neutral, acidic, or basic solution will arise. The ultimate solution pH will depend on a reaction between the solute and water.

- 1) In the Bronsted-Lowry model, acid base behavior is shown as a transfer of a proton.
- 2) A Bronsted acid must contain H in the formula and the H must be easily removed. The general formula is HA ex. H attached to highly electronegative atoms like the halogens, oxygen, or sulfur
- 3) A Bronsted base must contain a lone pair of electrons. The general formula is B ex. O^{2-} , OH^- , F^- , NH_3 and other N derivatives
- 4) In the Bronsted-Lowry model, a reaction between an acid and a base occurs to form a new acid and a new base. The acids and bases exist in pairs. When the acid loses a proton, it becomes a base and is called the conjugate base. When a base gains a proton, it becomes an acid and is called the conjugate acid.



- 5) When an acid is added to water, there is a Bronsted-Lowry acid base reaction where the acid behaves as an acid, and water acts as the base. This is the **acid ionization reaction**.



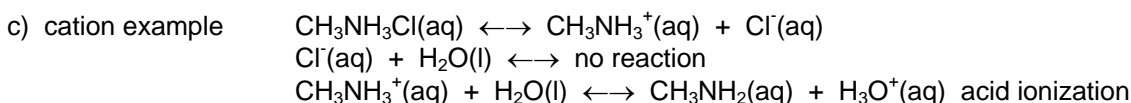
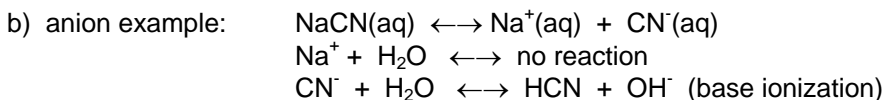
- 6) When a base is added to water, there is a Bronsted-Lowry acid base reaction where the base behave as a base and water acts as the acid. This is the **base ionization reaction**.

Be able to identify or provide the conjugate acids and conjugate bases of any acid or base. Remember, a conjugate base will have one less hydrogen than the acid and the conjugate acid will have one more hydrogen. Keep your charges straight. Remember the hydrogen is removed as a proton.

Categories of behavior of solutes in water – what are the major species in water

- 1) If a solute has strong covalent bonds there is no reaction between solute and water. The pH will be unchanged when the solute dissolves. These are molecules with no H in the formula or contain an H that will not come off easily such as that found in methanol (CH_3OH), ethanol (CH_3CH_2OH) or alkane chains such as butane ($CH_3CH_2CH_2CH_3$)
- 2) The solute is covalent and undergoes a reaction with water to produce a proton.
 - a) There is a complete reaction with water when the solute is a **strong acid** ($HClO_4$, H_2SO_4 , HNO_3 , HI , HBr , $HClO$) There will be no undissociated acid molecules left. The major species in solution after this reaction will be the conjugate base, H_3O^+ , the anion, and H_2O
$$HNO_3(aq) + H_2O(l) \rightarrow NO_3^-(aq) + H_3O^+(aq)$$
 - b) There is a partial reaction with water when the solute is a weak acid. **Any acid that is not a strong acid is considered to be a weak acid**. There will be an equilibrium and the major species in solution will be the weak acid and water. There will be small amounts of the conjugate base and the hydronium ion.
$$HF(aq) + H_2O(l) \longleftrightarrow F^-(aq) + H_3O^+(aq) \quad \text{(acid ionization)}$$
- 3) The solute is ionic. It will dissociate into ions and the component ions may undergo reaction with water.
 - a) Strong bases will dissociate to form OH^- . **Strong bases are the hydroxides of Group I and Group II metals**. ($NaOH$ and KOH are common strong bases. $LiOH$, $RbOH$, and $CsOH$ are less common strong bases. $Ca(OH)_2$, $Ba(OH)_2$ and $Sr(OH)_2$ will produce two moles OH^- per mole of solid). These strong bases will completely dissociate in water. The major species in water will be the metal ion, the hydroxide ion and water.

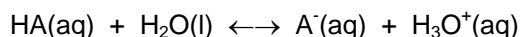
The reaction of interest is: $\text{OH}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{l}) + \text{OH}^-(\text{aq})$. Since there is no net change in the molecules present after the reaction, it is sufficient to know that the base dissociates in water.



Be able to write the chemical equations that show the acid base reaction of solutes in water.

Acid Ionization, K_a and $\text{p}K_a$

The acid ionization reaction is the transfer of a proton from the acid to water.



The equilibrium expression for this reaction is $K_{\text{eq}} = [\text{A}^-][\text{H}_3\text{O}^+]/[\text{HA}] = K_a$

For the acid ionization, K_{eq} is written K_a and is called the **acid dissociation constant**.

K_a values allow one to compare the strength of acids. Since it is an equilibrium constant, the larger the K_a , the more products there are, which means there will have been more dissociation of the acid and more protons formed. **Thus, the larger the K_a , the stronger the acid.** For strong acids, the reaction lies so far to the right that $[\text{HA}]$ is very small and it is difficult to determine the K_a accurately. However, comparing the values of weak acids is very useful.

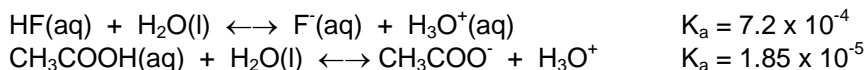
The p notation can be employed, such that $\text{p}K_a = -\log(K_a)$.

Note that the larger the K_a , the smaller the $\text{p}K_a$. Thus the stronger the acid, the smaller the $\text{p}K_a$.

Although we will discuss bases more later, a comment can be made now on the relative strength of bases. The relative strength of an acid is based on the extent to which it produces protons. The relative strength of a base depends on its affinity for a proton. The greater the affinity, the stronger the base.

In general, the stronger acid will produce a weaker conjugate base.

Consider:



In the first reaction there is a competition between H_2O and F^- for the proton.

In the second reaction there is a competition between H_2O and CH_3COO^- for the proton.

The first reaction lies further to the right than the second reaction. Thus water can steal the proton from F^- easier than from CH_3COO^- . Thus, F^- is the weaker base and HF is the stronger acid.

The take home message – the stronger the acid, the weaker the conjugate base or the weaker the base, the stronger the acid.

Be able to calculate K_a from $\text{p}K_a$ and vice versa. Be able to rank the strength of acids and conjugate bases if given K_a or $\text{p}K_a$ information.

Calculating the pH of Strong Acid Solutions:

In general, to determine the pH of a solution, the dominant equilibria must be identified. Strong acids dissociate completely. The major species in solution will be the proton and the conjugate base from the acid. What about the autoionization of water? This occurs to such a small extent that it can usually be ignored. Furthermore, the protons produced by the ionization of the strong acid will push the autoionization of water to the left because of Le Chatelier's principle. Thus, the major source of protons will be the acid.

The concentration of protons will be equal to the concentration of the strong acid.

What if two strong acids are mixed together? Each acid will completely dissociate and the total $[H^+]$ will be a sum from both sources.

What about the pH of a dilute concentration of a strong acid? Be careful. If the acid is really dilute, such as 1×10^{-7} or less, the contribution of water will be important. You won't have to work any problems of this type, just be aware of this fact.

Be able to determine the pH of a solution of a strong acid(s). If given the pH, be able to determine the concentration of the original acid.

Calculating the pH of Weak Acid Solutions:

The following steps will help you determine the pH of these solutions.

- 1) List the major species in solution
- 2) Identify the species that will produce protons and write the appropriate balanced equations
- 3) Determine if the contribution of any of the reactions is negligible.
- 4) Write the equilibrium expression for the dominant reaction.
- 5) Create an equilibrium reaction table. Include initial concentration, change and final concentration in terms of x .
- 6) Put values from the equilibrium table into the equilibrium expression (with K_a)
- 7) Simplify the equilibrium expression if possible (if x is small, check for perfect squares)
- 8) Solve for x
- 9) Check the assumption that x is small by using the 5% rule

Other comments:

- 1) How do you decide if some reactions are negligible? If the K_a is very small compared to other K_a s. For example, the K_a (K_w) for water is 1×10^{-14} . This is usually a factor of at least 1×10^6 times smaller than the K_a values for the weakest acids (for example, $K_a(\text{HOCl}) = 3.5 \times 10^{-8}$) and so the contribution of the ionization of water to the proton concentration can be ignored.
- 2) If the equilibrium expression cannot be simplified, the quadratic equation must be used. This would be the case if K_a was near 1×10^{-2} .
- 3) What is the 5% rule? (value of x /original concentration of acid) $\times 100$ must be less than 5
- 4) What if two weak acids are mixed together? Usually one will have a K_a significantly smaller than the other and the contribution to the protons concentration from the weaker acid can be ignored.
- 5) The percent dissociation is a way to describe how much acid has dissociated.
Percent dissociation = (amount of acid dissociated in M)/(amount of acid initially in M) $\times 100$
(Note the similarity of this to the 5% rule.)

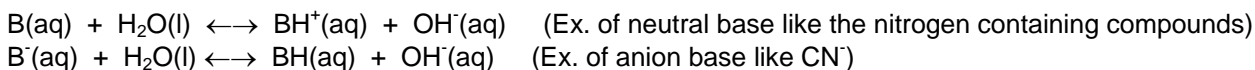
There are three values of importance in pH problems of weak acids, pH, initial acid concentration, and K_a . Given any two, you should be able to determine the third.

Be able to determine the pH of a weak acid solution. To do this, you would be given the initial concentration of the acid and the K_a .

If given the pH or percent dissociation and acid concentration, you should be able to determine the K_a .

Bases:

- 1) Strong bases are treated like strong acids. They completely dissociate in aqueous solution. The major species in solution will be the cation (conjugate acid, the hydroxide ion and water. The strong base will be the predominant source of hydroxide. The autoionization of water can be ignored. The concentration of hydroxide ion will be equal to the concentration of the strong base, when the metal ion is a Group I. **Remember that hydroxides of Group II metals will yield two moles of hydroxide per mole of base.**
- 2) Weak bases do not yield a hydroxide directly but undergo an acid base reaction with water to generate the hydroxide ion. This is the base ionization reaction. Water acts as an acid here.



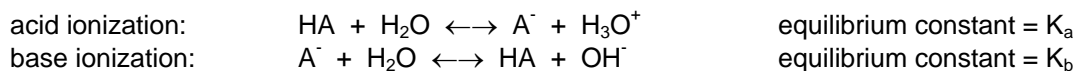
- a) The equilibrium for the reaction is equal to K_b , the base ionization constant.
 $K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$ for the first example.
- b) As with weak acids, where K_a is usually small, the K_b values are also small. As with weak acids, where the larger K_a indicates a stronger acid, a larger K_b indicates a stronger base.
- c) To determine the pH of a weak base solution, follow the steps as you did for weak acid solutions. **Remember that in these problems, x will be equal to the hydroxide concentration, not the proton concentration.** To avoid silly mistakes, be sure to write down the chemical reaction of interest. **Be sure to use the base ionization reaction for bases.**

Polyprotic Acids:

- 1) These acids have more than one acidic hydrogen. The hydrogens are released as protons, one at a time.
- 2) Each dissociation has its own K_a value.
- 3) Since the K_a values are usually quite different in magnitude, it will usually be the case, that all molecules will lose the first proton, before any lose a second proton.
- 4) The K_a value for dissociation of the first proton will be larger than the second K_a and the second larger than the third K_a if there is one.
- 5) Since the K_a values differ significantly, determining the pH of a polyprotic acid can be similar to that of a mix of two weak acids and only the dominant reaction will establish the pH.
- 6) The concentration of all species of acid can be determined.
- 7) Sulfuric acid is unique because the dissociation of the first proton is a strong acid, while the second is from a weak acid. The pH of the solution will be established by the first dissociation but the second equilibrium can be used to determine the concentration of SO_4^{2-} .

Acid-Base Properties of Salts:

- 1) There is a relationship between the base ionization constant and the acid ionization constant. Consider the acid HA and its conjugate base A^- .



- 2) The reactions can be added. When reactions are added together the equilibrium constants are multiplied. Thus the equilibrium constant for the net reaction is $K_a \times K_b$.
- 3) The net reaction is $2 \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_3\text{O}^+$. You should recognize this as the autoionization of water and the equilibrium constant for this is K_w .
- 4) Thus, $K_a \times K_b = K_w = 1 \times 10^{-14}$ and $\text{p}K_a + \text{p}K_b = 14$

General statements regarding the capacity of ions that are in salts to affect the pH

- 1) **Cations from a strong base** (group I and group II metals) will not affect the pH of the solution.
- 2) **Anions from strong acids** (conjugate bases) will not affect the pH of the solution. Thus, salts such as KCl, CaBr_2 , NaClO_4 , or $\text{Sr}(\text{NO}_3)_2$ will not change the pH.

- 3) **Anions from weak acids** (conjugate bases). Being conjugate bases of weak acids, these have a significant affinity for protons and will undergo base ionization. In base ionization, a hydroxide is formed and anions of this type produce basic solutions. Salts of this type would contain a cation from 1 above, such as KNO_2 , NaCN , RbF .

The reaction of interest would be: $\text{NO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longleftrightarrow \text{HNO}_2(\text{aq}) + \text{OH}^-(\text{aq})$

- 4) **Cations from weak bases** (conjugate acids) These are acids and will undergo acid ionization. Many of these are nitrogen containing molecules. Salts of this type would include an anion from 2 above, such as NH_4Br .

The important part of solving this type of problem is being able to identify if you have a conjugate base or a conjugate acid. Once you can do that, treat the problem as a weak acid problem or a weak base problem. Be sure to use the appropriate ionization (acid or base). Be sure to use the corresponding equilibrium constant, K_a if an acid or K_b if a base. Note, that you will usually be given the K_a or K_b for the parent acid or base. In these problems you are dealing with conjugate bases and conjugate acids so you will have to use $K_a \times K_b = K_w$ to get the appropriate value.

- 5) If a salt contains an anion, conjugate base, from a weak acid AND a cation, conjugate acid, from a weak base, both will have the capacity to undergo ionization reactions. **Compare the K_b for the base present and the K_a for the acid present.** If the K_b is larger than the K_a , the solution will be basic. If K_a is larger than the K_b the solution will be acidic. If the ionization constants are nearly equal, the solution will have a pH of near 7. Examine 14.21
- 6) A salt containing a highly charged metal will be acidic. The metal pulls on the electrons on the water oxygen, thus weakening the hydrogen oxygen bond and the hydrogen is released.

Be able to predict whether dissolving a salt in water will give an acidic, basic, or neutral solution. Be able to calculate the pH of a salt solution.

The Effect of Structure on Acid-Base Properties:

Without knowing the actual $\text{p}K_a$ values, the relative strength of acids can be predicted based on structure.

Consider: $\text{HA} + \text{H}_2\text{O} \longleftrightarrow \text{A}^- + \text{H}_3\text{O}^+$

- 1) Acid ionization involves breaking the bond between H and the A. The weaker the bond, the stronger the acid.
- 2) When the hydrogen leaves as a proton, it leaves the electrons of the bond behind, thus the more electronegative A is, the stronger the acid.

When comparing acid strength **across a period**, factor two is more important. If you compare HF, H_2O , and NH_3 , the electronegativities are $F = 4.0$, $O = 3.5$, and $N = 3.0$. We would predict that HF is the strongest acid.

When comparing acid strength **down a group**, factor one is more important. Acid strength will increase as you go down a group. Why is this? Atomic radii increases down a group. The further apart two atoms are, the weaker the bond, the weaker the bond, the stronger the acid. Thus, as you compare, H_2O , H_2S , H_2Se , and H_2Te , the weakest bond is H_2Te , which will be the strongest acid.

- 3) Electronegativity is important in relative strength of oxyacids. Addition of electronegative groups (halogens or oxygens) onto the central atom will make the acid stronger. Addition of electron repelling groups, such as CH_3 or CH_3CH_2 will make the acid weaker. CH_3CH_2 is more repelling than CH_3 which is more repelling than H.

Compare: H-O-H and Cl-O-H Cl is more electronegative so the second is a stronger acid

Compare: HCOOH and CH_3COOH CH_3 is more repelling than H so the first is a stronger acid

Compare: CH_3COOH , CH_2BrCOOH CH_2Br will be more electronegative than CH_3 so the second is a stronger acid

Compare: O-Cl-OH , $\text{O}_2\text{-Cl-OH}$, $\text{O}_3\text{-Cl-OH}$ The third has more electronegative ions so is the strongest acid.

- 4) What about bases? Since a base has to share electrons, the stronger base will have less electronegative groups or electron repelling groups. CH_3NH_2 is a better base than NH_3 since CH_3 is more repelling than H.
- 4) Highly charged metals pull on oxygen and result in an acidic solution. The more charged the metal, the stronger the acid.

Given a group of related compounds, be able to predict which is the strongest or weakest acid.

Acid-Base Properties of Oxides:

This was covered in an earlier quarter. The oxides of metals usually form bases, and the oxides of non-metals usually form acids. The exception to this is for highly charged metals. They will usually form acids.

Be able to predict if a solution would be acidic or basic upon the dissolution of an oxide.

The Lewis Acid-Base Model:

A Lewis acid is an electron pair acceptor. A Lewis base is an electron pair donor.

If given a reaction, be able to identify the acid or the base or predict if a compound would act as a Lewis acid or base.