

## Chapter 16 Acid and Bases

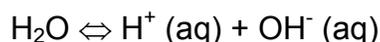
### I. Acidic and Basic water solutions:

#### A. Dissociation of water

The  $\text{H}^+$  ion (or the  $\text{H}_3\text{O}^+$  ion) is characteristic of acidic water solutions.

The  $\text{OH}^-$  ion gives basic solutions their characteristic properties.

There is an equilibrium between these two ions in water or in any aqueous solution:



We can write the equilibrium constant expression:

$$K_c = [\text{H}^+] [\text{OH}^-] / [\text{H}_2\text{O}]$$

in all aqueous solutions, the concentration of water is essentially the same, about 1000/18.0 or 55 mol/liter. Therefore,  $[\text{H}_2\text{O}]$  can be combined with  $K_c$  to give a new constant  $K_w$ , **the dissociation constant of water**.

$$K_w = [\text{H}^+] [\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

Since water dissociates into equal amounts of these two ions, we can calculate the concentrations of  $\text{H}^+$  and  $\text{OH}^-$  ions.

$$\begin{aligned} [\text{H}^+] &= [\text{OH}^-] \\ [\text{H}^+] [\text{OH}^-] &= [\text{H}^+]^2 = 1.0 \times 10^{-14} \end{aligned}$$

$$[\text{H}^+] = 1.0 \times 10^{-7} = [\text{OH}^-]$$

Any aqueous solution where  $[\text{H}^+] = [\text{OH}^-]$  is called a *neutral* solution.

Normally, they are not equal. However, as the concentration of one increases, the other must decrease. In other words,  $[\text{H}^+] [\text{OH}^-] = 1.0 \times 10^{-14}$  at  $25^\circ\text{C}$  remains constant. If we then know the concentration of one, we can find the other.

Acidic  $[\text{H}^+] > 1.0 \times 10^{-7}$

Basic  $[\text{OH}^-] > 1.0 \times 10^{-7}$

## B. pH

pH is defined as *power of the hydrogen ion* and is defined

$$\text{pH} = -\log [\text{H}^+] = \log_{10} 1/[\text{H}^+]$$

examples:

$$[\text{H}^+] = 1 \times 10^{-4}$$

$$\text{pH} = -\log_{10} (1 \times 10^{-4}) = -(-4.0) = 4.0$$

$$[\text{H}^+] = 1 \times 10^{-7}$$

$$\text{pH} = -\log_{10} (1 \times 10^{-7}) = -(-7.0) = 7.0$$

$$[\text{H}^+] = 1 \times 10^{-10}$$

$$\text{pH} = -\log_{10} (1 \times 10^{-10}) = -(-10.0) = 10.0$$

notice the pattern?

See table 16.2 for surprising pH values of common substances.

## C. pOH

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

$$\text{pOH} + \text{pH} = 14$$

## D. Indicators

We have used indicators in titrations to indicate a change in pH level or the endpoint. In a titration, when a solution is at the point where moles one ion = moles of another, the pH changes. Using the correct indicator for where the endpoint is reached is important. Table 19.3 gives pH ranges for common indicators.

## II. General Models of Acids, Bases and Acid-Base reactions.

### A. Arrhenius

Simply stated any substance that forms  $\text{H}^+$  ions in water solution are acidic and those that form  $\text{OH}^-$  ions are basic.

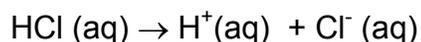
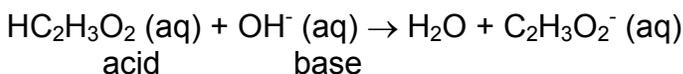
His theory is very limiting.

### B. Bronsted-Lowry

A *proton transfer* occurs from one species to another.

Acid: the species that gives up the proton ( $\text{H}^+$ )

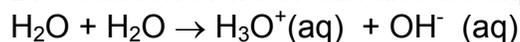
Base: the molecule or ion that accepts the  $\text{H}^+$  is a base.



There doesn't appear to be a proton acceptor even though HCl is an acid.  
The proton acceptor is really water.

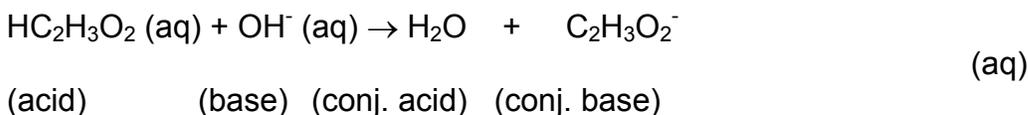


Dissociation of water can also be expressed this way.



### Conjugate acid-conjugate base

Acid + Base  $\leftrightarrow$  Conjugate base + conjugate acid



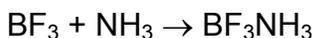
looking at the forward,  $\text{HC}_2\text{H}_3\text{O}_2$  donates the proton and is therefore the acid. In the reverse, water is the donator and therefore a conjugate acid.

### C. Lewis Concept

Bronsted-Lowry is restricted in that the reaction must involve proton transfer to be classified.

Acid: accepts an electron pair

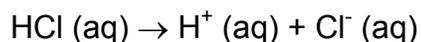
Base: donates an electron pair



draw this structurally to see what happens.

## III. Strong and Weak Acids

### A. Strong acids completely dissociate in water. (strong electrolyte)



There are only a few common strong acids: LEARN THESE!



### B. Weak acids are partially dissociated in water.

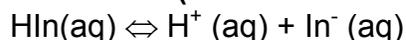


Species that act as weak acids:

#### 1. Molecules containing an ionizable hydrogen

phosphoric, pyruvic, hydrofluoric, nitrous, lactic, acetic, carbonic, hydrogen sulfide, hypochlorous, and hydrogen cyanide.

## 2. Acid-base indicators (contains ionizable hydrogen molecule)

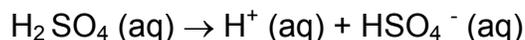


HIn has one color where In<sup>-</sup> has another.

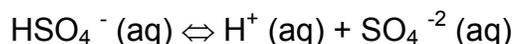
The position of the equilibrium is sensitive to [H<sup>+</sup>]. When [H<sup>+</sup>] is high, the equilibrium shift to the left and we see its color yellow. When [H<sup>+</sup>] is low, the equilibrium shifts to the right and we see blue.

## 3. Anions containing an ionizable hydrogen atom

Look at the dissociation of the strong acid H<sub>2</sub>SO<sub>4</sub>

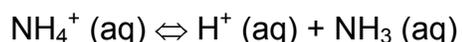


The anion remaining contains a H that can be dissociated. But, HSO<sub>4</sub><sup>-</sup> is classified as a weak acid.



## 4. Cations

The ammonium cation, NH<sub>4</sub><sup>+</sup> behaves as a weak acid in water:



*Most metal cations, except those of group 1 metals and Ca<sup>2+</sup>, Sr<sup>2+</sup>, and Ba<sup>2+</sup>, are weak acids.*

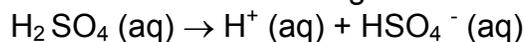
How can a cation like Zn<sup>2+</sup> make an acidic solution?

When ZnCl<sub>2</sub> is added to water, the cation Zn(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> is formed. It then slightly dissociates in water as follows: Zn(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> ⇌ H<sup>+</sup> (aq) + Zn(H<sub>2</sub>O)<sub>3</sub>(OH)<sup>+</sup>

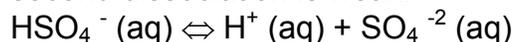
## 5. Polyprotic acids

Certain species contain more than one ionizable hydrogen. Polyprotic means many proton acids. Polyprotic can be strong or weak:

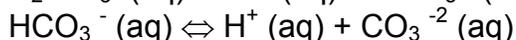
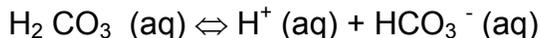
first dissociation is strong :



second dissociation is weak:



Both first and second dissociation weak:



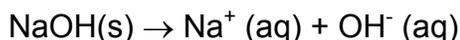
The first dissociation occurs to a greater extent since it is easier to remove a charged ion ( $\text{H}^+$ ) from a neutral molecule than from a negative ion. This is generally true for all polyprotic acids; essentially all of the  $\text{H}^+$  ions come from the first dissociation.

### C. Determining Experimentally

Measure electrical conductivities of solutions. 0.10M HF will have low conductivity since small amount of ions to conduct a current. 0.10M HCl has a high conductivity, 10 times that of HF.

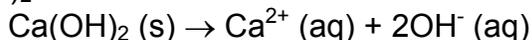
## IV. Strong and Weak Bases

**A. Strong bases, like strong acids, dissociate completely in water.** (strong electrolyte)



Strong bases are limited to

1. The hydroxides of group 1 metals
2. The hydroxides of the heavier group 2 elements,  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ , and  $\text{Ba}(\text{OH})_2$



### B. Weak Bases

Weak bases do not furnish  $\text{OH}^-$  ions directly by dissociation. They are generated by the reaction of a weak base with water.



the forward reaction occurs only to a slight extent. Nearly 99% of the molecules of  $\text{NH}_3$  remain unreacted. If we start with 0.10M solution  $\text{NH}_3$  we would end with 0.099M  $\text{NH}_3$  and 0.001M  $\text{OH}^-$  and 0.001M  $\text{NH}_4^+$ . The pH of the solution would be 11.

Most weak bases are anions.

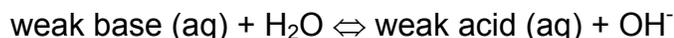


Again, the forward reaction is slight but enough to have a basic solution.

In weak base reactions, the following two products are formed:

- a weak acid ( $\text{NH}_4^+$ , HF)
- an  $\text{OH}^-$  ion which makes the solution basic.

The general reaction is:



*The stronger the acid, the weaker its conjugate base; the stronger base, the weaker its conjugate acid.*

Table 16.7 p584

## V Acid- Base Properties of Salt Solutions

At this point you should be able to classify a solution of  $\text{NH}_3$  as basic or  $\text{H}_2\text{SO}_4$  as acidic. What about NaCl,  $\text{NaNO}_2$  or  $\text{NH}_4\text{I}$ ?

These are salts. salts are classified as an ionic compound containing a cation other than  $\text{H}^+$  and an anion other than  $\text{OH}^-$  or  $\text{O}^{2-}$

Salts will completely dissociate into ions in water. Acid-Base properties of salts are determined by the behavior of their ions. Some ions have no effect on pH; some do.

### A. Neutral ions

Neutral ions do not affect pH. Neutral anions are derived from strong acids

Neutral cations are derived from strong bases

### B. Basic Anions:

any anion that is derived from a weak acid acts as a weak base in water solution.

### C. Acidic Ions

All cations except those of the alkali metals and the heavier alkaline earth's

the  $\text{HSO}_4^-$  and  $\text{H}_2\text{PO}_4^-$  anions

A procedure to explain whether a salt solution is acidic or basic:

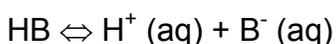
1. Determine what ions are present. (cation and anion)

2. *Decide whether each ion is acidic, basic or neutral.*
3. *Decide whether the salt will be acidic, basic or neutral.* If both cation and anion are neutral, the salt is neutral. If one is acidic and the other neutral, salt is acidic. If one basic and one neutral, the salt is basic. If one is basic and one acidic, it is impossible to predict the salt.
4. *Write the net ionic equations for the reaction of each acidic or basic.*

## VI. Acid-Base Equilibria

### I. Equilibrium constant for the dissociation of a weak acid, $K_a$

Remember, weak acids only slightly dissociate:



The products are a proton and a conjugate base. Since the reactants are in equilibrium with the products, we can write an equilibrium expression:

$$K_a = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]}$$

$K_a$  is called the *ionization constant* or *acid dissociation constant* of the weak acid HB.

the concentrations that appear in  $K_a$  expressions are as always *equilibrium concentrations in moles per liter*.

$K_a$  values are a measure of the extent to which the acid dissociates in water. **The smaller the dissociation constant, the weaker the acid.** Table 20.1 in your text (page 611) has some  $K_a$  values.

The decreasing  $K_a$  means less dissociation. What does it mean in regards to pH?

In comparing the dissociation constants of weak acids, we sometimes use the term  $\text{p}K_a$  which **is analogous to pH**.

$$\text{p}K_a = -\log_{10} K_a$$

the larger the value of  $\text{p}K_a$ , the weaker the acid.

*Example 1: Acetylsalicylic acid, more commonly known as aspirin, is a weak organic acid whose formula we will represent as Hasp. A water solution is prepared by dissolving 0.100 mole Hasp per liter. The concentration of  $\text{H}^+$  in this solution is found to be 0.0057 mol/L. Calculate  $K_a$  and  $\text{p}K_a$  for the solution.*

**Percent dissociation** can also be used to describe the acidity of solution of a weak acid in water. It is defined as the percentage of weak acid molecules originally present that dissociate to form  $H^+$  ions.

$$\text{percent dissociation HB} = \frac{[H^+]}{\text{orig. conc. HB}} \times 100$$

In example 1, what would the percent dissociation of Hasp be?

### **VII Determination of $[H^+]$ in solutions of weak acids.**

In a solution prepared by dissolving a weak acid, HB, in water:

$$[H^+] = [B^-]$$

$$[HB] = \text{orig. conc. HB} - [H^+]$$

*Example 2:*

*Nicotinic acid,  $C_6H_5O_2N$  ( $K_a = 1.4 \times 10^{-5}$ ) is another name for niacin, an important vitamin. Determine  $[H^+]$  in a solution prepared by dissolving 0.10 mol nicotinic acid, Hnic, to form 1 liter solution.*

\* In general,  $K_a$  is seldom known to be better than  $\pm 5\%$ . Therefore, in the expression  $K_a = x^2 / (a-x)$  you can neglect  $x$  in the denominator if doing so does not induce an error of more than 5%.

if  $x/a = \text{percent dissociation}/100 \leq 0.05$   
then we can take  $a-x = a$

But, you know there will be a case where this doesn't hold.

*Example 3:*

*Calculate  $[H^+]$  in a 0.100M solution of nitrous acid  $HNO_2$ , for which  $K_a = 4.5 \times 10^{-4}$ .*

*1. The method of successive approximations:*

*2. The quadratic formula*

**VIII. Equilibrium Constant for Reaction of a Weak base with Water,  $K_b$**



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

Again, the larger the  $K_b$  the stronger the base.

### A. Relation between $K_a$ and $K_b$

$K_a$  decreases,  $K_b$  increases.

Lets derive the relation: (p600)

$$K_a \times K_b = K_w$$

### B. Determination of $[\text{OH}^-]$ in a solution of weak base.

*Example 8: For the butyrate ion,  $\text{But}^-$ ,  $K_b$  is  $5.0 \times 10^{-10}$ . For a 1.0 M solution of sodium butyrate,  $\text{NaBut}$ , calculate*

*a.  $[\text{OH}^-]$                       b.  $[\text{H}^+]$                       c. pH*

## IX. Relations Between Equilibrium Constants

### A. Forward and Reverse Reactions

We can calculate the equilibrium constant,  $K$ , for a reaction if we know the equilibrium constant  $K'$  for the reverse reaction.

$$K = 1/K'$$

Suppose we want to know  $K$  for the neutralization reaction

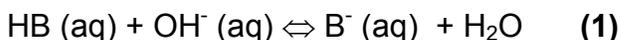


recall, the reverse reaction:  $\text{H}_2\text{O} (\text{aq}) \rightleftharpoons \text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq})$   $K_w = 1 \times 10^{-14}$

$K$  for the neutralization rxn should then be the reciprocal:  $1 \times 10^{14}$ .

The fact that  $K$  is so large indicates this reaction goes to completion which is what happens in strong acid- strong base reactions.

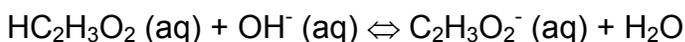
Now, consider the reaction with a weak acid,  $\text{HB}$  and a strong base,  $\text{NaOH}$ .



This is simply the reverse reaction of the weak base  $\text{B}^-$  with water. This equilibrium constant is  $K_b$ . Therefore, for rxn (1)

$$K = 1 / (K_b \text{ of } \text{B}^-)$$

Let's look at the reaction of acetic acid with sodium hydroxide.



$$K = 1 / K_b \text{ C}_2\text{H}_3\text{O}_2^- = 1 / 5.6 \times 10^{-10} = 1.8 \times 10^9$$

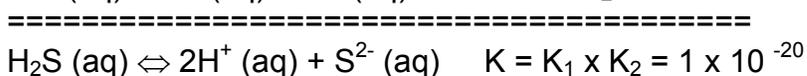
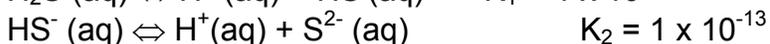
Since  $K$  is a very large number, we can conclude that the reaction of a weak acid with a strong base should go to completion. The same will also be true of a strong acid-weak base.

## B. Rule of Multiple Equilibria

***If the reaction can be expressed as the sum of two other reactions,  $K$  for the overall reaction is the product of the equilibrium constants for the individual reactions.***

Example:

The stepwise dissociation of the weak polyprotic acid  $\text{H}_2\text{S}$ .



## C. Summarizing the results for finding the equilibrium constant of a rxn:

1. Check to see if the constant you want is directly available from a table ( $K_a$  or  $K_b$ )
2. If the constant is not listed for the reaction, examine the equation carefully. Will the reverse reaction give you a value where you can then apply the reciprocal rule?
3. If neither (1) nor (2) apply, you will need to use the rule of multiple equilibria. Express the given equation as the sum of two or more equations. Find the equilibrium constants for each using the reciprocal rule if necessary. Finally, use the rule of multiple equilibria to find  $K$ .

## X. Acid-Base Reactions

### A. Reactions of Strong Acids with Strong Bases

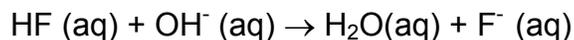
Consider mixing NaOH and HNO<sub>3</sub>. Since they are strong acid and base, both will completely dissociate into ions. The acid base reaction that occurs involves the H<sup>+</sup> FROM HNO<sub>3</sub> and the OH<sup>-</sup> from NaOH. The net ionic equation is:



This is the net ionic equation for any reaction between a strong acid and a strong base. It is called a **neutralization reaction**. A pH of 7.0 will result. (Note, we do not include the spectator ions.)

### B. Reactions of Weak Acid and Strong Base

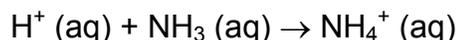
Consider NaOH and HF. NaOH will completely dissociate, HF will barely. the equation for the reaction will be



Recall, anions derived from weak acids (like HF) are themselves weak bases. Therefore, this reaction will show a slightly basic result instead of neutral.

### C. Strong Acid and Weak Base

HCl added to NH<sub>3</sub>. The acid completely dissociates, the base ,barely. The resulting net ionic reaction:



Recall, the ammonium ion is a weak acid. Hence, the final solution may be slightly acidic.

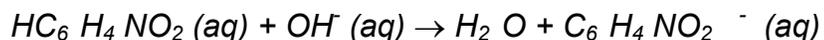
*When writing net ionic equations, YOU MUST KNOW WHAT IS WEAK AND WHAT IS STRONG TO PREDICT THE PRODUCTS AS WELL AS pH.*

## XI. Acid-Base Titrations

Acid base titrations can be used to

1. Find the concentrations of an acid or base by comparison to a "standardized" acid or base.
2. Find the percentage of an acid or base component.

*Example 1: A research chemist isolates a sample of nicotinic acid , HC<sub>6</sub> H<sub>4</sub> NO<sub>2</sub> (molar mass = 123 g/mol) To determine its purity, she titrates 0.450 g of the sample with 0.100M NaOH. She finds that 36.2 mL NaOH is required . the reaction is:*



*Assuming any impurity present does not react with the base, calculate*

1. *the mass in grams of nicotinic acid in the sample*
2. *the mass percent of nicotinic acid in the sample*

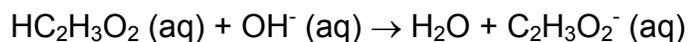
## A. Indicators in Acid Base Titrations

Indicators are used to tell at what point the reaction is complete, when equivalent quantities of acid and base have been used. This is the equivalence point.

To determine what indicator to use, you first need to perform the titration with a pH probe. A graph of pH Vs volume of titrant. At the equivalence point, the pH will change steeply and then level off as excess titrant is added.

### 1. Weak Acid with Strong Base

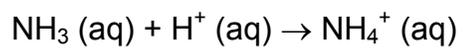
1.00 M acetic acid with 1.00 M NaOH.



$\text{C}_2\text{H}_3\text{O}_2^-$  causes it to be basic\*. The pH of the endpoint is approx. 9. Phenolphthalein would be a good indicator since it changes around 8. Methyl red would not be good since it would change at a pH of 5.

### 2. Strong Acid with Weak Base

1.00 M  $\text{NH}_3$  and 1.00 M HCl



$\text{NH}_4^+$  causes a slightly acid solution at the endpoint\*. the pH is around 5. Methyl red would be good for this titration.

### **3. Strong Acid with Strong Base**

1.00 M HCl and 1.00 M NaOH

pH would be 7 at the endpoint. Bromthymol blue would be a good choice.