

AP Chemistry Notes

**Chapter 14 Acids and Bases**

<u>Due</u>	<u>Assignments</u>
	Ch14.1 19,20,21,23,25,26,29
	Ch14.2 35-37,39-44
	Ch14.3 45-49all,51,53
	Ch14.4 55,56,59,60, 61-67odd ,68
	Ch14.5 69,70,71-79odd
	Ch14.6 83-87all,89-97odd
	Ch14.7 105-109all,111,112
	Ch14.8 113-129odd
	Ch14.9 131-141odd

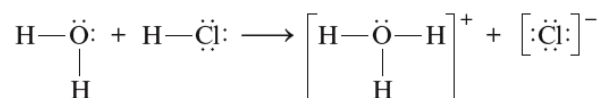
## 14.1 The Nature of Acids and Bases

Acids were first recognized as a class of substances that *taste sour*.

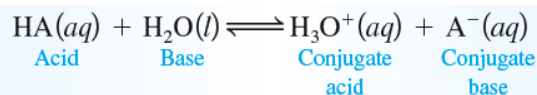
Bases, sometimes called *alkalis*, are characterized by their *bitter taste and slippery feel*.

**Arrhenius Concept-** *acids produce hydrogen ions in aqueous solution, while bases produce hydroxide ions. Limited because it applies only to aqueous solutions and allows for only one kind of base.*

**Brønsted–Lowry model**, an acid is a proton ( $\text{H}^+$ ) donor, and a base is a proton acceptor.



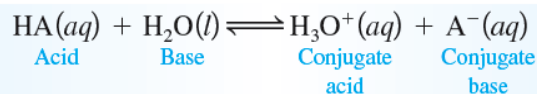
Note that the proton is transferred from the HCl molecule to the water molecule to form  $\text{H}_3\text{O}^+$ , which is called the **hydronium ion**\*



**Conjugate Base** is everything that remains of the acid molecule after a proton is lost.

**Conjugate Acid** is formed when the proton is transferred to the base.

**Conjugate Acid–Base Pair** consists of two substances related to each other by the donating and accepting of a single proton. Look for the species that are off by 1  $\text{H}^+$ .



The equilibrium expression for the reaction is

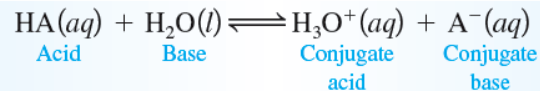
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

(Both  $\text{H}_3\text{O}^+_{(aq)}$  and  $\text{H}^+_{(aq)}$  are commonly used to represent the hydrated proton.)

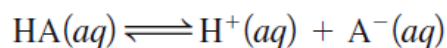
**$K_a$**  is called the **acid dissociation constant**.

This reaction needs to be looked at like a competition for the  $\text{H}^+$  between water and the conjugate base. Whichever species gets the  $\text{H}^+$  is the stronger base.

If  $\text{H}_2\text{O}$  is a much stronger base than  $\text{A}^-$ , that is, if  $\text{H}_2\text{O}$  has a much greater affinity for  $\text{H}^+$  than does  $\text{A}^-$ , the equilibrium position will be far to the right; most of the acid dissolved will be in the ionized form. Conversely, if  $\text{A}^-$  is a much stronger base than  $\text{H}_2\text{O}$ , the equilibrium position will lie far to the left. In this case most of the acid dissolved will be present at equilibrium as HA.



In a dilute solution we can assume that the concentration of liquid water remains essentially constant when an acid is dissolved. Thus the term  $[\text{H}_2\text{O}]$  is not included in the equilibrium expression, and  $K_a$  has the same form as that for the simple dissociation into ions:



We can leave out the water, but don't forget that the  $\text{H}^+$  is really hydronium  $\text{H}_3\text{O}^+$ .

### Acid Dissociation (Ionization) Reactions

Write the simple dissociation (ionization) reaction (omitting water) for each of the following acids.

a. hydrochloric acid ( $\text{HCl}$ )

b. acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ )

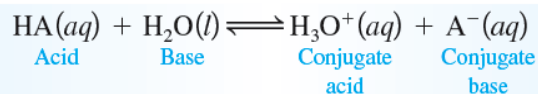
c. the ammonium ion ( $\text{NH}_4^+$ )

d. the anilinium ion ( $\text{C}_6\text{H}_5\text{NH}_3^+$ )

e. the hydrated aluminum(III) ion  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$

## 14.2 Acid Strength

The strength of an acid is defined by the equilibrium position of its dissociation (ionization) reaction:



A **strong acid** is one for which this equilibrium lies far to the right. This means that almost all the original HA is dissociated (ionized) at equilibrium.

A *strong acid yields a weak conjugate base*—one that has a low affinity for a proton. A strong acid also can be described as an acid whose conjugate base is a much weaker base than water.

A *weak acid* is one for which the equilibrium lies far to the left. Most of the acid originally placed in the solution is still present as HA at equilibrium. A weak acid dissociates only to a very small extent in aqueous solution. A weak acid has a conjugate base that is a much stronger base than water. The weaker the acid, the stronger its conjugate base.

### Strong Acids

sulfuric acid,  $\text{H}_2\text{SO}_{4(aq)}$ ,

hydrochloric acid,  $\text{HCl}_{(aq)}$ ,

hydrobromic acid,  $\text{HBr}_{(aq)}$ ,

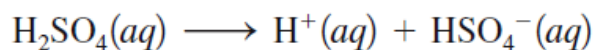
hydroiodic acid,  $\text{HI}_{(aq)}$ ,

nitric acid,  $\text{HNO}_{3(aq)}$ ,

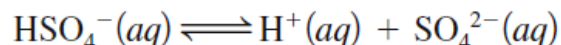
perchloric acid,  $\text{HClO}_{4(aq)}$

Sulfuric acid is actually a **diprotic acid**, an acid having two acidic protons.

The acid  $\text{H}_2\text{SO}_4$  is a strong acid, virtually 100% dissociated (ionized) in water:



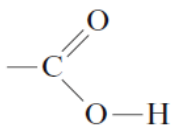
The  $\text{HSO}_4^-$  ion, however, is a weak acid:



(This becomes important when  $\text{H}_2\text{SO}_4$  is at low concentrations.)

Most acids are **oxyacids**, in which the acidic proton is attached to an oxygen atom. There are exceptions like HCl.

**Organic acids**, those with a carbon atom backbone, commonly contain the **carboxyl group**.



Acids of this type are usually weak. Examples are acetic acid ( $\text{CH}_3\text{COOH}$ ), often written  $\text{HC}_2\text{H}_3\text{O}_2$ , and benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ).

**Monoprotic acids**- those acids having one acidic proton

Strong Acids have very large  $K_a$  values and are not listed below. Just know them.

Formula	Name	Value of $K_a^*$
$\text{HSO}_4^-$	Hydrogen sulfate ion	$1.2 \times 10^{-2}$
$\text{HClO}_2$	Chlorous acid	$1.2 \times 10^{-2}$
$\text{HC}_2\text{H}_2\text{ClO}_2$	Monochloroacetic acid	$1.35 \times 10^{-3}$
HF	Hydrofluoric acid	$7.2 \times 10^{-4}$
$\text{HNO}_2$	Nitrous acid	$4.0 \times 10^{-4}$
$\text{HC}_2\text{H}_3\text{O}_2$	Acetic acid	$1.8 \times 10^{-5}$
$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$	Hydrated aluminum(III) ion	$1.4 \times 10^{-5}$
HOCl	Hypochlorous acid	$3.5 \times 10^{-8}$
HCN	Hydrocyanic acid	$6.2 \times 10^{-10}$
$\text{NH}_4^+$	Ammonium ion	$5.6 \times 10^{-10}$
$\text{HOC}_6\text{H}_5$	Phenol	$1.6 \times 10^{-10}$

↑  
Increasing acid strength

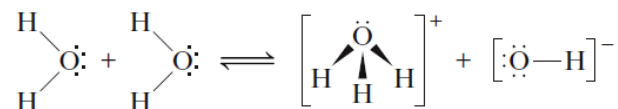
## Relative Base Strength

Using the  $K_a$  Table (make them acids by adding an  $H^+$ ), arrange the following species according to their strengths as bases (reverse order from acid strength (water is between strong and weak)):

$H_2O$ ,  $F^-$ ,  $Cl^-$ ,  $NO_2^-$ , and  $CN^-$ .

## Water as an Acid and a Base

A substance is said to be **amphoteric** if it can behave either as an acid or as a base. Water is the most common **amphoteric substance**. We can see this clearly in the **autoionization** of water, which involves the transfer of a proton from one water molecule to another to produce a hydroxide ion and a hydronium ion:



In this reaction, one water molecule acts as an acid by furnishing a proton, and the other acts as a base by accepting the proton.

The autoionization reaction for water  $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

leads to the equilibrium expression  $K_w = [H_3O^+][OH^-] = [H^+][OH^-]$

where  $K_w$ , called the **dissociation constant for water**. At  $25^\circ\text{C}$  in pure water,

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

$$\begin{aligned} K_w &= [H^+][OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) \\ &= 1.0 \times 10^{-14} \end{aligned}$$

a neutral solution, where  $[H^+] = [OH^-]$   
an acidic solution, where  $[H^+] > [OH^-]$   
a basic solution, where  $[OH^-] > [H^+]$

$K_w$  is temperature dependent. at  $37^\circ\text{C}$ ,  $K_w = 2.42 \times 10^{-14}$

$$\begin{aligned} [H^+][OH^-] &= 2.42 \times 10^{-14} \\ [H^+] &= [OH^-] = 1.55 \times 10^{-7} \end{aligned}$$

So the pH for a neutral solution at  $37^\circ\text{C}$  is 6.81.

### Calculating $[H^+]$ and $[OH^-]$

Calculate  $[H^+]$  or  $[OH^-]$  as required for each of the following solutions at  $25^\circ\text{C}$ , and state whether the solution is neutral, acidic, or basic.

a.  $1.0 \times 10^{-5} \text{ M OH}^-$

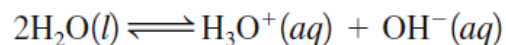
b.  $1.0 \times 10^{-7} \text{ M OH}^-$

c.  $10.0 \text{ M H}^+$

### Autoionization of Water

At  $60^\circ\text{C}$ , the value of  $K_w$  is  $1 \times 10^{-13}$

Using Le Châtelier's principle, predict whether the reaction is exothermic or endothermic.



Calculate  $[H^+]$  and  $[OH^-]$  in a neutral solution at  $60^\circ\text{C}$ .

### 14.3 The pH Scale

The pH scale provides a convenient way to represent solution acidity.

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

Ex.

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

$$\text{pH} = -(-7.00) = 7.00$$

Sig. Figs.\*\*\* *The number of decimal places in the log is equal to the number of significant figures in the original number.*

$$[\text{H}^+] = 1.0 \times 10^{-9} \text{ M}$$

↖ 2 significant figures

$$\text{pH} = 9.00$$

↖ 2 decimal places

Similar log scales are used for representing other quantities; for example,

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

The pH changes by 1 for every power of 10 change in  $[\text{H}^+]$ . For example, a solution of pH 3 has an  $\text{H}^+$  concentration 10 times that of a solution of pH 4 and 100 times that of a solution of pH 5.

Also note that because pH is defined as  $-\log[\text{H}^+]$ , *the pH decreases as  $[\text{H}^+]$  increases.*

#### Calculating pH and pOH

Calculate pH and pOH for each of the following solutions at 25°C.

a.  $1.0 \times 10^{-3} \text{ M OH}^-$

b.  $1.0 \text{ M OH}^-$



## Calculations Using pH

The pH of a sample of human blood was measured to be 7.41 at 25°C. Calculate pOH,  $[H^+]$ , and  $[OH^-]$  for the sample.

### 14.4 Calculating the pH of Strong Acid Solutions

\*\*\*Autoionization of water is important if the concentration of a strong acid is less than  $10^{-7}M$ . For typical concentrations this contribution can be disregarded.

Strong acids ionize 100%

#### pH of Strong Acids

a. Calculate the pH of 0.10 M  $HNO_3$ .

b. Calculate the pH of  $1.0 \times 10^{-10} M HCl$ .

**Did you notice what just happen?**

### 14.5 Calculating the pH of Weak Acid Solutions

\*\*Use the acid with the larger  $K_a$  value if 2 are present, to determine the dominate source of  $H^+$ .

Determine the pH of 1.0 M HF ( $K_a = 7.2 \times 10^{-4}$ )

## The pH of Weak Acids

The hypochlorite ion ( $\text{OCl}^-$ ) is a strong oxidizing agent often found in household bleaches and disinfectants. It is also the active ingredient that forms when swimming pool water is treated with chlorine. In addition to its oxidizing abilities, the hypochlorite ion has a relatively high affinity for protons (it is a much stronger base than  $\text{Cl}^-$ , for example) and forms the weakly acidic hypochlorous acid ( $\text{HOCl}$ ,  $K_a = 3.5 \times 10^{-8}$ ).

Calculate the pH of a 0.100-M aqueous solution of hypochlorous acid.

### The pH of Weak Acid Mixtures

Calculate the pH of a solution that contains 1.00 M HCN ( $K_a = 6.2 \times 10^{-10}$ ) and 5.00 M HNO<sub>2</sub> ( $K_a = 4.0 \times 10^{-4}$ ). Also calculate the concentration of cyanide ion (CN<sup>-</sup>) in this solution at equilibrium.

## Percent Dissociation

$$\text{Percent dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \times 100\%$$

*For a given weak acid, the percent dissociation increases as the acid becomes more dilute.*

## Calculating Percent Dissociation

Calculate the percent dissociation of acetic acid ( $K_a = 1.8 \times 10^{-5}$ ) in each of the following solutions:

**a. 1.00 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>**

**b. 0.100 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>**

### Calculating $K_a$ from Percent Dissociation

Lactic acid ( $\text{HC}_3\text{H}_5\text{O}_3$ ) is a chemical that accumulates in muscle tissue during exertion. In a 0.100-M aqueous solution, lactic acid is 3.7% dissociated. Calculate the value of  $K_a$  for this acid.

## 14.6 Bases

Arrhenius concept, a base is a substance that produces  $\text{OH}^-$  ions in aqueous solution.

All the hydroxides of the Group 1 elements ( $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{RbOH}$ , and  $\text{CsOH}$ ) are strong bases, but only  $\text{NaOH}$  and  $\text{KOH}$  are common laboratory reagents, because the lithium, rubidium, and cesium compounds are expensive. The alkaline earth (Group 2) hydroxides— $\text{Ca(OH)}_2$ ,  $\text{Ba(OH)}_2$ , and  $\text{Sr(OH)}_2$ —are also strong bases. For these compounds, 2 moles of hydroxide ion are produced for every mole of metal hydroxide dissolved in aqueous solution.

### The pH of Strong Bases

Calculate the pH of a  $5.0 \times 10^{-2} M$   $\text{NaOH}$  solution.

Calculate the pH of a  $5.0 \times 10^{-2} M$   $\text{Ca(OH)}_2$  solution.

### Weak Bases

$K_b$  always refers to the reaction of a base with water to form the conjugate acid and the hydroxide ion.



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

Name	Formula	Conjugate Acid	$K_b$
Ammonia	$\text{NH}_3$	$\text{NH}_4^+$	$1.8 \times 10^{-5}$
Methylamine	$\text{CH}_3\text{NH}_2$	$\text{CH}_3\text{NH}_3^+$	$4.38 \times 10^{-4}$
Ethylamine	$\text{C}_2\text{H}_5\text{NH}_2$	$\text{C}_2\text{H}_5\text{NH}_3^+$	$5.6 \times 10^{-4}$
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_6\text{H}_5\text{NH}_3^+$	$3.8 \times 10^{-10}$
Pyridine	$\text{C}_5\text{H}_5\text{N}$	$\text{C}_5\text{H}_5\text{NH}^+$	$1.7 \times 10^{-9}$

### **The pH of Weak Bases I**

Calculate the pH for a 15.0-M solution of  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ).

### **The pH of Weak Bases II**

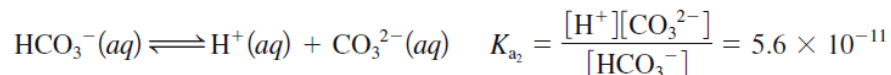
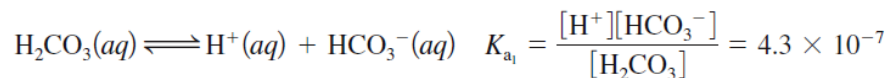
Calculate the pH of a 1.0-M solution of methylamine ( $K_b = 4.38 \times 10^{-4}$ ).



## 14.7 Polyprotic Acids

Some important acids, such as sulfuric acid ( $\text{H}_2\text{SO}_4$ ), carbonic acid ( $\text{H}_2\text{CO}_3$ ), and phosphoric acid ( $\text{H}_3\text{PO}_4$ ), can furnish more than one proton and are called polyprotic acids.

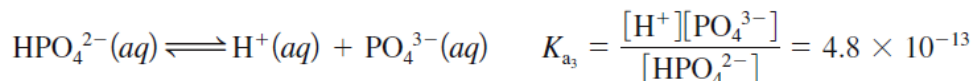
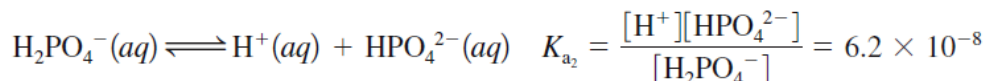
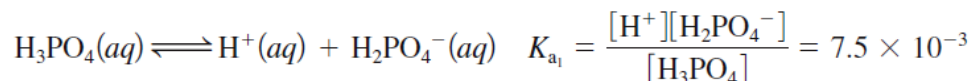
### Carbonic Acid



The successive  $K_a$  values for the dissociation equilibria are designated  $K_{a_1}$  and  $K_{a_2}$ .

\*\*\*The conjugate base  $\text{HCO}_3^-$  of the first dissociation equilibrium becomes the acid in the second step.

Phosphoric acid is a triprotic acid (three protons) that dissociates in the following steps:



For a typical weak polyprotic acid,

$$K_{a_1} > K_{a_2} > K_{a_3}$$

The acid involved in each step of the dissociation is successively weaker.

Name	Formula	$K_{a_1}$	$K_{a_2}$	$K_{a_3}$
Phosphoric acid	$\text{H}_3\text{PO}_4$	$7.5 \times 10^{-3}$	$6.2 \times 10^{-8}$	$4.8 \times 10^{-13}$
Arsenic acid	$\text{H}_3\text{AsO}_4$	$5.5 \times 10^{-3}$	$1.7 \times 10^{-7}$	$5.1 \times 10^{-12}$
Carbonic acid	$\text{H}_2\text{CO}_3$	$4.3 \times 10^{-7}$	$5.6 \times 10^{-11}$	
Sulfuric acid	$\text{H}_2\text{SO}_4$	Large	$1.2 \times 10^{-2}$	
Sulfurous acid	$\text{H}_2\text{SO}_3$	$1.5 \times 10^{-2}$	$1.0 \times 10^{-7}$	
Hydrosulfuric acid*	$\text{H}_2\text{S}$	$1.0 \times 10^{-7}$	$\sim 10^{-19}$	
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	$6.5 \times 10^{-2}$	$6.1 \times 10^{-5}$	
Ascorbic acid (vitamin C)	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	$7.9 \times 10^{-5}$	$1.6 \times 10^{-12}$	

Generally, the first dissociation step makes an important contribution to  $[\text{H}^+]$ .

### **The pH of a Polyprotic Acid**

Calculate the pH of a 5.0-M  $\text{H}_3\text{PO}_4$  solution and the equilibrium concentrations of the species  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ .

## 14.8 Acid–Base Properties of Salts

### *Salts That Produce Neutral Solutions*

Salts that consist of the cations of strong bases and the anions of strong acids have no effect on  $[H^+]$  when dissolved in water. This means that aqueous solutions of salts such as KCl, NaCl,  $NaNO_3$ , and  $KNO_3$  are neutral (have a pH of 7).

### *Salts That Produce Basic Solutions*

The conjugate base a weak acid has a significant affinity for a proton and will attack water for the  $H^+$ , leaving  $OH^-$ . You will be given a  $K_a$  when you have a basic salt.

$$K_a \times K_b = K_w$$

$$K_b = \frac{K_w}{K_a}$$

### Salts as Weak Bases

Calculate the pH of a 0.30-M NaF solution. The  $K_a$  value for HF is  $7.2 \times 10^{-4}$ .

### *Salts That Produce Acidic Solutions*

Salts in which the anion is not a base and the cation is the conjugate acid of a weak base produce acidic solutions.

The conjugate acid a weak base has no affinity for a proton and will give it up to water for the leaving  $\text{H}_3\text{O}^+$ . You will be given a  $K_b$  when you have an acidic salt.

$$K_a = \frac{K_w}{K_b}$$

### **Salts as Weak Acids I**

Calculate the pH of a 0.10-M  $\text{NH}_4\text{Cl}$  solution. The  $K_b$  value for  $\text{NH}_3$  is  $1.8 \times 10^{-5}$ .



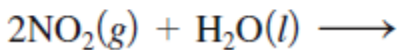
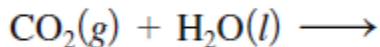
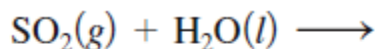
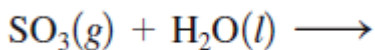
## 14.10 Acid–Base Properties of Oxides

H-O-X can behave as an acid or a base.

If X has a relatively high electronegativity, the O-X bond will be covalent and strong. When the compound containing the H-O-X grouping is dissolved in water, the O-X bond will remain intact. It will be the polar and relatively weak H-O bond that will tend to break, releasing a proton. We have an acid.

On the other hand, if X has a very low electronegativity, the O-X bond will be ionic and subject to being broken in polar water.

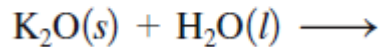
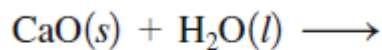
Covalent Oxide in water (Add them together in your head)



Thus when a covalent oxide dissolves in water, an acidic solution forms.

Ionic Oxides in water (reverse water and add them in your head)

when an ionic oxide dissolves in water, a basic solution results



### 14.11 The Lewis Acid–Base Model

A Lewis acid is an electron-pair acceptor, and a Lewis base is an electron-pair donor.

