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5.111 Principles of Chemical Science  
Fall 2008

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## 5.111 Lecture Summary #21

Acid-Base Equilibrium      Read Chapter 10

Topics: Classification of Acid-Bases, Autoionization of Water, pH Function, Strength of Acids and Bases, Equilibrium Involving Weak Acids.

Classification of Acids and Bases1. Arrhenius - a narrow definition of acids and bases

An **acid** is a substance that when dissolved in water increases the concentration of hydrogen ions.  
A **base** is a substance that increases the hydroxide concentration.

2. Brønsted-Lowry - a broader definition

A Brønsted-Lowry **acid** - a substance that can donate a hydrogen ion

A Brønsted-Lowry **base** - a substance that can accept a hydrogen ion

Example 1



(note: hydronium ion  $\text{H}_3\text{O}^+$  (aq) is used instead of  $\text{H}^+$  (aq) to represent the true nature of hydrogen ions in water)

Acid-bases occur as **conjugate acid-base pairs**.  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  are a pair.  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  are a pair. The conjugate base of an acid is the base that is formed when the acid has donated a hydrogen ion. The conjugate acid of a base is the acid that forms when base accepts a hydrogen ion.

Example 2 Which are Brønsted-Lowry acids and which are Brønsted-Lowry bases?



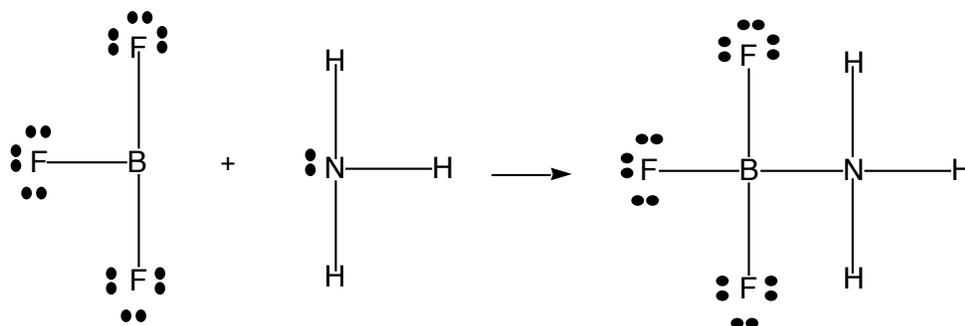
**amphoteric** - molecules that can function either as acids or bases depending on the reaction conditions.

### 3. Lewis Acid and Base - more general definition - applies to reactions that don't involve a hydrogen ion

Lewis **base** - species that donates lone-pair electrons

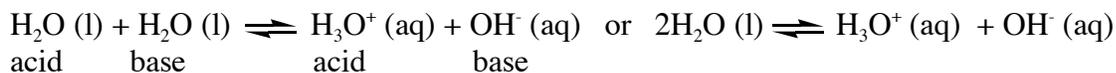
Lewis **acid** - species that accepts such electrons

Example 1



Ammonia is the Lewis base. It donates lone-pair electrons to BF<sub>3</sub>, the Lewis acid and the electron acceptor.

### Autoionization of Water



How much H<sub>2</sub>O is in a glass of water?

$$\begin{aligned} \Delta G^\circ &= \Delta G_f^\circ(\text{H}_3\text{O}^+, \text{aq}) + \Delta G_f^\circ(\text{OH}^-, \text{aq}) - 2\Delta G_f^\circ(\text{H}_2\text{O}, \text{l}) \\ &= (-237.13) + (-157.24) - 2 \times (-237.13) \text{ kJ/mol} \\ &= +79.89 \text{ kJ/mol} \end{aligned}$$

$$\ln K = -\Delta G^\circ/RT = \frac{-(79.89 \times 10^3 \text{ J/mol})}{(8.3145 \text{ J/Kmol})(298.0 \text{ K})} = -32.24$$

$$K = 1.0 \times 10^{-14} \text{ at } 298 \text{ K}$$

This very small value indicates that only a small proportion of water molecules are ionized. Concentration of ions due to autoionization of water is very low, about 1 molecule in 200 million.

$$K = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \text{This } K \text{ is called } K_w.$$

Because  $K_w$  is an equilibrium constant, the product of  $[\text{H}_3\text{O}^+][\text{OH}^-]$  is always  $1.0 \times 10^{-14}$  at 298 K.

Note: Because the concentration of the solvent,  $\text{H}_2\text{O}$ , does not change significantly in a dilute solution, it does not enter the equilibrium expression. The solvent, water, is very nearly pure, and pure liquids and pure solids are not included in equilibrium expressions.

### pH Function

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

### pOH Function

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

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$\log K_w = \log[\text{H}_3\text{O}^+] + \log[\text{OH}^-]$$

$$-\log K_w = -\log[\text{H}_3\text{O}^+] - \log[\text{OH}^-]$$

$$\text{p}K_w = \text{pH} + \text{pOH} = 14.00 \text{ at } 25^\circ\text{C}$$

### Strength of Acids and Bases

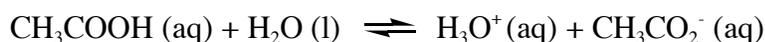
$$\text{pH of pure water } \text{pH} = -\log (1.0 \times 10^{-7}) = 7.00$$

pH of an acid solution is

pH of a base solution is

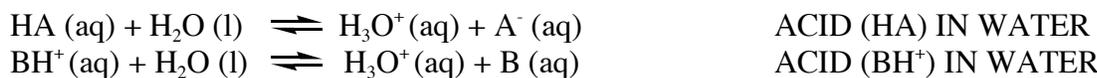
EPA defines waste as "corrosive" if the pH is lower than 3.0 or higher than 12.5.

#### 1. Acid in water



$$\text{Acid ionization constant } K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{COOH}]}$$

$K_a$  equals  $1.76 \times 10^{-5}$  at  $25^\circ\text{C}$ . Small value tells us that only a small proportion of  $\text{CH}_3\text{COOH}$  molecules donate their proton when dissolved in water (weak acid).



A strong acid has a  $K_a > 1$  which means that the acid ionizes almost completely.

A weak acid has a  $K_a < 1$ . The reaction with water does not produce many ionized species before equilibrium is reached.

$$\text{p}K_a = -\log K_a$$

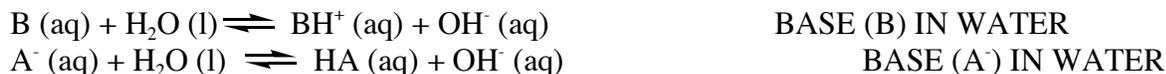
The lower the value of  $K_a$ , the higher the value of  $\text{p}K_a$ . The higher the  $\text{p}K_a$ , the weaker the acid.

## 2. Base in water



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

$K_b$  is  $1.8 \times 10^{-5}$  at  $25^\circ\text{C}$ . This small value tells us that only a small amount of  $\text{NH}_3$  ionizes to  $\text{NH}_4^+$  and  $\text{OH}^-$  in solution. A strong base reacts essentially completely to give  $\text{OH}^-$  (aq) when put in water.  $\text{NH}_3$  is not a strong base. It is a moderately weak base.



$$\text{p}K_b = -\log K_b$$

larger  $K_b$ , stronger base

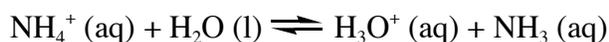
larger  $\text{p}K_b$ , weaker base

## 3. Conjugate acids and bases

The stronger the acid, the weaker its conjugate base.

The stronger the base, the weaker its conjugate acid.

Consider conjugate acid-base pair  $\text{NH}_3$  and  $\text{NH}_4^+$ :

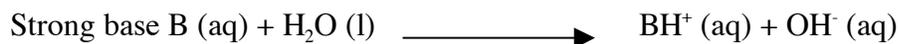


Multiply  $K$ 's together and get:

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

$$K_a \times K_b = K_w$$

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



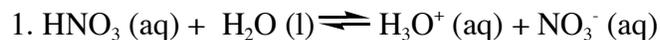
#### 4. Relative strengths of acids

Is  $\text{HNO}_3$  or  $\text{NH}_4^+$  a stronger acid? Will the reaction lie far to the right or left?

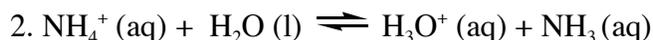


$$K = \frac{[\text{NO}_3^-][\text{NH}_4^+]}{[\text{HNO}_3][\text{NH}_3]}$$

consider each acid separately:



$$K_a (\text{HNO}_3) = \frac{[\text{H}_3\text{O}^+][\text{NO}_3^-]}{[\text{HNO}_3]} = 20.$$



$$K_a (\text{NH}_4^+) = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = 5.6 \times 10^{-10}$$

Subtract equation 2 from 1 and divide the corresponding equilibrium constants.

$$K = \frac{K_a (\text{HNO}_3)}{K_a (\text{NH}_4^+)} = \frac{\frac{[\text{H}_3\text{O}^+][\text{NO}_3^-]}{[\text{HNO}_3]}}{\frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}} = \frac{[\text{NO}_3^-][\text{NH}_4^+]}{[\text{HNO}_3][\text{NH}_3]} = \frac{20.}{5.6 \times 10^{-10}} = 3.6 \times 10^{10}$$

Reaction lies far to the \_\_\_\_\_.  $\text{HNO}_3$  is a \_\_\_\_\_ than  $\text{NH}_4^+$ .

Types of acid-base problems

1. weak acid in water
2. weak base in water  $\leftarrow$  salt in water
3. strong acid in water
4. strong base in water
5. buffer

Equilibrium involving weak acids

Example: Vitamin C (ascorbic acid,  $\text{HC}_6\text{H}_7\text{O}_6$ ) has a  $K_a$  of  $8.0 \times 10^{-5}$ . Calculate the pH of a solution made by dissolving 500. mg in 100. mL of water.

$$0.500 \text{ g} \times 1 \text{ mol}/176.126 \text{ g} = 2.84 \times 10^{-3} \text{ mol}$$

$$2.84 \times 10^{-3} \text{ mol}/0.100 \text{ L} = 0.0284 \text{ M}$$



	$\text{HC}_6\text{H}_7\text{O}_6$	$\text{H}_3\text{O}^+$	$\text{C}_6\text{H}_7\text{O}_6^-$
initial molarity	0.0284	0	0
change in molarity	-x	+x	+x
equilibrium molarity	0.0284 - x	+x	+x

$$K_a = 8.0 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_7\text{O}_6^-]}{[\text{HC}_6\text{H}_7\text{O}_6]} = \frac{x^2}{0.0284 - x}$$

If  $x \ll 0.0284$ , then  $(0.0284 - x) \approx 0.0284$ .

$$K_a = 8.0 \times 10^{-5} = \frac{x^2}{0.0284}$$

$$x = 0.00151 \text{ (really 2 sf, but carry extra)}$$

Check assumption. Is  $0.0284 - 0.00151 \approx 0.0284$ ?

You can use assumption if  $x$  is less than 5% of the value in question.

Here  $(0.00151/0.0284) \times 100\% = 5.3\%$  (more than 5%), so must use the quadratic equation.

Using quadratic eq,  $x = 0.00147$  (really 2 sf)

$$\text{pH} = -\log [1.47 \times 10^{-3}] = 2.83$$