

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

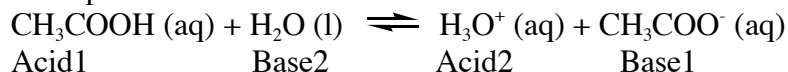
An **acid** is a substance that when dissolved in water increases the concentration of hydrogen ions.
A **base** is a substance that increases the hydroxide concentration.

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 H_3O^+ (aq) is used instead of H^+ (aq) to represent the true nature of hydrogen ions in water)

Acid-bases occur as **conjugate acid-base pairs**. CH_3COOH and CH_3COO^- are a pair. H_2O and H_3O^+ 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?



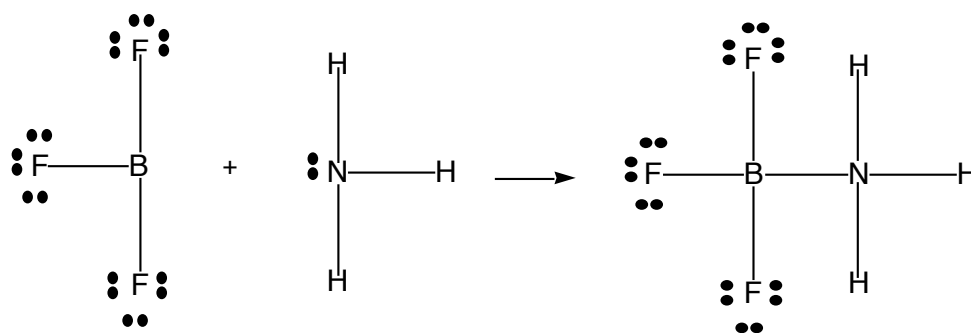
amphoteric - molecules that can function either as acids or bases depending on the reaction conditions.

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

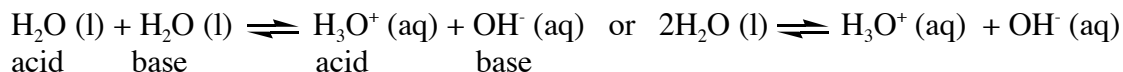
Lewis **acid** - species that accepts such electrons

Example 1



Ammonia is the Lewis base. It donates lone-pair electrons to BF_3 , the Lewis acid and the electron acceptor.

Autoionization of Water



How much H_2O 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 1.0×10^{-14} at 298 K.

Note: Because the concentration of the solvent, H_2O , 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

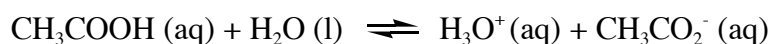
$$\text{pH of pure water } \text{pH} = -\log (1.0 \times 10^{-7}) = 7.00$$

pH of an acid solution is

pH of a base solution is

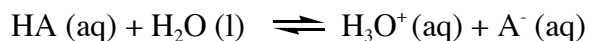
EPA defines waste as "corrosive" if the pH is lower than 3.0 or higher than 12.5.

1. Acid in water

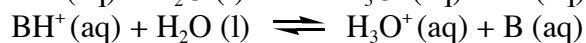


$$\text{Acid ionization constant } K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{COOH}]}$$

K_a equals 1.76×10^{-5} at 25°C . Small value tells us that only a small proportion of CH_3COOH molecules donate their proton when dissolved in water (weak acid).



ACID (HA) IN WATER

ACID (BH⁺) IN WATER

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.

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

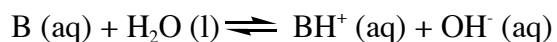
The lower the value of K_a , the higher the value of $\text{p}K_a$. The higher the $\text{p}K_a$, the weaker the acid.

2. Base in water



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

K_b is 1.8×10^{-5} at 25°C. This small value tells us that only a small amount of NH_3 ionizes to NH_4^+ and OH^- in solution. A strong base reacts essentially completely to give OH^- (aq) when put in water. NH_3 is not a strong base. It is a moderately weak base.



BASE (B) IN WATER

BASE (A⁻) IN WATER

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

larger K_b , stronger base

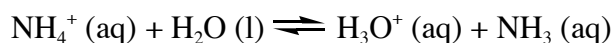
larger $\text{p}K_b$, weaker base

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 NH_3 and NH_4^+ :

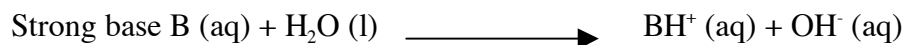
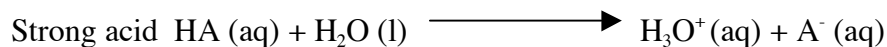


Multiply K 's together and get:

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

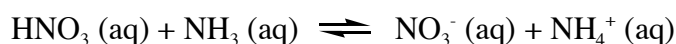
$$K_a \times K_b = K_w$$

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



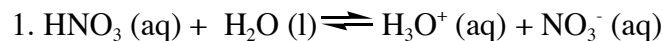
4. Relative strengths of acids

Is HNO_3 or NH_4^+ a stronger acid? Will the reaction lie far to the right or left?

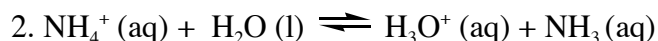


$$K = \frac{[\text{NO}_3^-][\text{NH}_4^+]}{[\text{HNO}_3][\text{NH}_3]}$$

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 _____. HNO_3 is a _____ than NH_4^+ .

Types of acid-base problems

1. weak acid in water
2. weak base in water \longleftrightarrow 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 8.0×10^{-5} . Calculate the pH of a solution made by dissolving 500. mg in 100. mL of water.

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

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



	$\text{HC}_6\text{H}_7\text{O}_6$	H_3O^+	$\text{C}_6\text{H}_7\text{O}_6^-$
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)

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

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