

Objectives

- Explain the meaning of pH and pOH.
- Relate pH and pOH to the ion product constant for water.
- Calculate the pH and pOH of aqueous solutions.

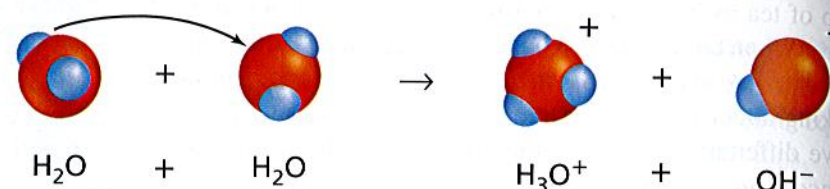
Vocabulary

ion product constant for water
pH
pOH

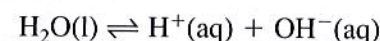
Water not only serves as the solvent in solutions of acids and bases, it also plays a role in the formation of the ions. In aqueous solutions of acids and bases, water sometimes acts as an acid and sometimes as a base. You can think of the self-ionization of water as an example of water assuming the role of an acid and a base in the same reaction.

Ion Product Constant for Water

Recall from Section 19.1 that pure water contains equal concentrations of H^+ and OH^- ions produced by self-ionization. One molecule of water acts as a Brønsted-Lowry acid and donates a hydrogen ion to a second water molecule. The second molecule of water accepts the hydrogen ion and becomes a hydronium ion. The 1:1 ratio between the products means that equal numbers of hydronium ions and hydroxide ions are formed.



The equation for the equilibrium can be simplified in this way.



The double arrow indicates that this is an equilibrium. Recall that the equilibrium constant expression is written by placing the concentrations of the products in the numerator and the concentrations of the reactants in the denominator. In this example, all terms are to the first power because all the coefficients are 1.

$$K_{\text{eq}} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

The concentration of pure water is constant so it can be combined with K_{eq} by multiplying both sides of the equation by $[\text{H}_2\text{O}]$.

$$K_{\text{eq}}[\text{H}_2\text{O}] = K_w = [\text{H}^+][\text{OH}^-]$$

The result is a special equilibrium constant expression that applies only to the self-ionization of water. The constant, K_w , is called the ion product constant for water. The **ion product constant for water** is the value of the equilibrium constant expression for the self-ionization of water. Experiments show that in pure water at 298 K, $[\text{H}^+]$ and $[\text{OH}^-]$ are both equal to $1.0 \times 10^{-7} \text{M}$. Therefore, at 298 K, the value of K_w is 1.0×10^{-14} .

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

$$K_w = 1.0 \times 10^{-14}$$

The product of $[\text{H}^+]$ and $[\text{OH}^-]$ always equals 1.0×10^{-14} at 298 K. This means that if the concentration of H^+ ion increases, the concentration of OH^- ion must decrease. Similarly, an increase in the concentration of OH^- ion causes a decrease in the concentration of H^+ ion. You can think about these changes in terms of Le Châtelier's principle, which you learned about in Chapter 18. Adding extra hydrogen ions to the self-ionization of water at equilibrium is a stress on the system. The system reacts in a way to relieve the stress. The added H^+ ions react with OH^- ions to form more water molecules. Thus, the concentration of OH^- ion decreases. Example Problem 19-1 shows how you can use K_w to calculate the concentration of either the hydrogen ion or the hydroxide ion if you know the concentration of the other ion.

EXAMPLE PROBLEM 19-1

Using K_w to Calculate $[\text{H}^+]$ and $[\text{OH}^-]$

At 298 K, the H^+ ion concentration of an aqueous solution is $1.0 \times 10^{-5} \text{M}$. What is the OH^- ion concentration in the solution? Is the solution acidic, basic, or neutral?

1. Analyze the Problem

You are given the concentration of H^+ ion and you know that K_w equals 1.0×10^{-14} . You can use the ion product constant expression to solve for $[\text{OH}^-]$. Because $[\text{H}^+]$ is greater than 1.0×10^{-7} , you can predict that $[\text{OH}^-]$ will be less than 1.0×10^{-7} .

Known

$$[\text{H}^+] = 1.0 \times 10^{-5} \text{M}$$

$$K_w = 1.0 \times 10^{-14}$$

Unknown

$$[\text{OH}^-] = ? \text{ mol/L}$$

2. Solve for the Unknown

Write the ion product constant expression.

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

Isolate $[\text{OH}^-]$ by dividing both sides of the equation by $[\text{H}^+]$.

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

Substitute K_w and $[\text{H}^+]$ into the expression and solve.

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1.0 \times 10^{-9} \text{ mol/L}$$

Because $[\text{H}^+] > [\text{OH}^-]$, the solution is acidic.

3. Evaluate the Answer

The answer is correctly stated with two significant figures because $[\text{H}^+]$ and K_w each have two. As predicted, the hydroxide ion concentration, $[\text{OH}^-]$, is less than $1.0 \times 10^{-7} \text{ mol/L}$.



The hydrogen ion and hydroxide ion concentrations of these familiar vegetables are the same as the concentrations calculated in this Example Problem.

PRACTICE PROBLEMS

18. The concentration of either the H^+ ion or the OH^- ion is given for three aqueous solutions at 298 K. For each solution, calculate $[\text{H}^+]$ or $[\text{OH}^-]$. State whether the solution is acidic, basic, or neutral.
- $[\text{H}^+] = 1.0 \times 10^{-13} \text{M}$
 - $[\text{OH}^-] = 1.0 \times 10^{-7} \text{M}$
 - $[\text{OH}^-] = 1.0 \times 10^{-3} \text{M}$

Practice!
For more practice calculating $[\text{H}^+]$ and $[\text{OH}^-]$ from K_w , go to **Supplemental Practice Problems** in Appendix A.

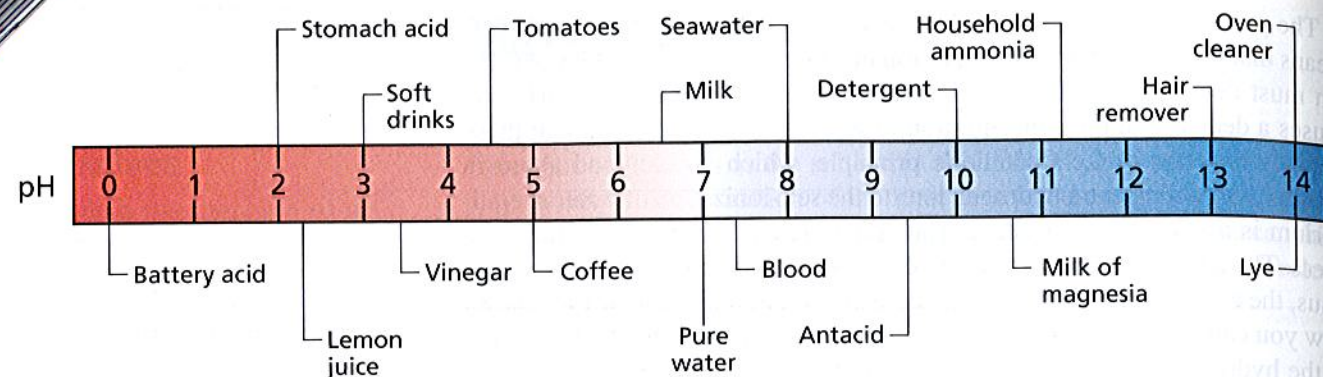


Figure 19-11

Which has the higher concentration of hydrogen ion, sea water or detergent? How many times higher?

pH and pOH

As you have probably noted, concentrations of H^+ ions are often small numbers expressed in exponential notation. Because these numbers are cumbersome, chemists adopted an easier way to express H^+ ion concentrations using a pH scale based on common logarithms. The **pH** of a solution is the negative logarithm of the hydrogen ion concentration.

$$pH = -\log [H^+]$$

At 298 K, acidic solutions have pH values below 7. Basic solutions have pH values above 7. Thus, a solution having a pH of 0.0 is strongly acidic; a solution having a pH of 14.0 is strongly basic; and a solution with pH = 7.0 is neutral. The logarithmic nature of the pH scale means that a change of one pH unit represents a tenfold change in ion concentration. A solution having a pH of 3.0 has ten times the hydrogen ion concentration of a solution with a pH of 4.0. The pH scale and pH values of some common substances are shown in Figure 19-11.

EXAMPLE PROBLEM 19-2

Calculating pH from $[H^+]$

What is the pH of a solution with a hydronium ion $[H^+]$ concentration of $3.0 \times 10^{-6} M$?

Known

$$[H^+] = 3.00 \times 10^{-6} M$$

$$pH = -\log [H^+]$$

$$pH = -\log [3.00 \times 10^{-6}]$$

$$pH = 5.52$$

Unknown

$$pH = ?$$

3. Evaluate the Answer

Values for pH are expressed with as many decimal places as the number of significant figures in the H^+ ion concentration. Thus, the pH is correctly stated with two decimal places. As predicted, the pH value is 7.00.

PRACTICE PROBLEMS

19. Calculate the pH of solutions having the following ion concentrations at 298 K.

- $[H^+] = 1.0 \times 10^{-2} M$
- $[H^+] = 3.0 \times 10^{-6} M$
- $[OH^-] = 8.2 \times 10^{-6} M$

Using pOH Sometimes chemists find it convenient to express the basicity, or alkalinity, of a solution on a pOH scale that mirrors the relationship between pH and $[H^+]$. The **pOH** of a solution is the negative logarithm of the hydroxide ion concentration.

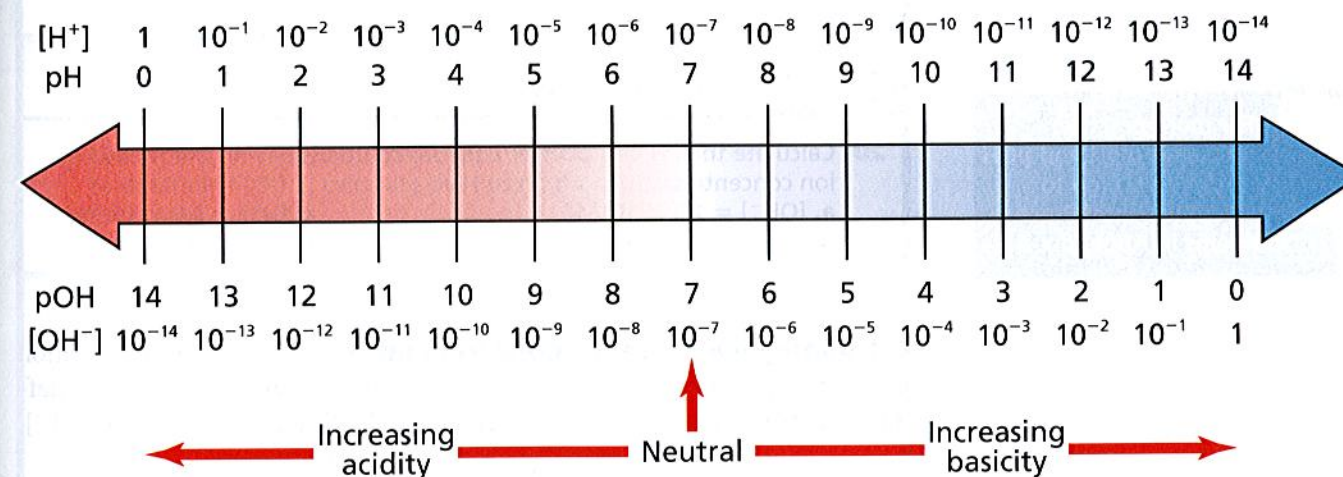
$$pOH = -\log [OH^-]$$

At 298 K, a solution having a pOH less than 7.0 is basic; a solution having a pOH of 7.0 is neutral; and a solution having a pOH greater than 7.0 is acidic. As with the pH scale, a change of one pOH unit expresses a tenfold change in ion concentration. For example, a solution with a pOH of 2.0 has 100 times the hydroxide ion concentration of a solution with a pOH of 4.0.

A simple relationship between pH and pOH makes it easy to calculate either quantity if the other is known.

$$pH + pOH = 14.00$$

Figure 19-12 illustrates the relationship between pH and $[H^+]$ and the relationship between pOH and $[OH^-]$ at 298 K. Use this diagram as a reference until you become thoroughly familiar with these relationships.

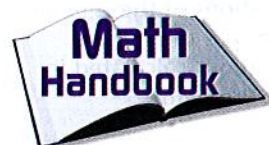


Practice! For more practice calculating pH, go to Supplemental Practice Problems in Appendix A.

Try at Home LAB See page 961 in Appendix E for Testing for Ammonia

Figure 19-12

Study this diagram to sharpen your understanding of pH and pOH. Note that at each vertical position, the sum of pH (above the arrow) and pOH (below the arrow) equals 14. Also note that at every position the product of $[H^+]$ and $[OH^-]$ equals 10^{-14} .



Review logarithms in the Math Handbook on page 910 of this text.

EXAMPLE PROBLEM 19-3

Calculating pOH and pH from $[\text{OH}^-]$

An ordinary household ammonia cleaner is an aqueous solution of ammonia gas with a hydroxide-ion concentration of $4.0 \times 10^{-3}M$. Calculate pOH and pH of a typical cleaner at 298 K.

1. Analyze the Problem

You have been given the concentration of hydroxide ion and must calculate pOH and pH. First, you must calculate pOH using the definition of pOH. Then, pH can be calculated using the relationship $\text{pH} + \text{pOH} = 14.00$. The negative log of 10^{-3} (the power of 10 of the hydroxide ion concentration) is 3. Therefore, pOH should be close to 3 and pH should be close to 11 or 12.

Known	Unknown
$[\text{OH}^-] = 4.0 \times 10^{-3}M$	pOH = ?
	pH = ?

2. Solve for the Unknown

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

Substitute $4.0 \times 10^{-3}M$ for $[\text{OH}^-]$ in the equation.

$$\text{pOH} = -\log (4.0 \times 10^{-3})$$

$$\text{pOH} = -(\log 4.0 + \log 10^{-3})$$

Log tables or your calculator indicate $\log 4.0 = 0.60$ and $\log 10^{-3} = -3$. Substitute these values in the equation.

$$\text{pOH} = -[0.60 + (-3)] = -(0.60 - 3) = 2.40$$

The pOH of the solution is 2.40.

Solve the equation $\text{pH} + \text{pOH} = 14.00$ for pH by subtracting pOH from both sides of the equation.

$$\text{pH} = 14.00 - \text{pOH}$$

Substitute the value of pOH.

$$\text{pH} = 14.00 - 2.40 = 11.60$$

The pH of the solution is 11.60.

3. Evaluate the Answer

The values of pH and pOH are correctly expressed with two decimal places because the given concentration has two significant figures. As predicted, pOH is close to 3 and pH is close to 12.

PRACTICE PROBLEMS

20. Calculate the pH and pOH of aqueous solutions having the following ion concentrations.

a. $[\text{OH}^-] = 1.0 \times 10^{-6}M$

c. $[\text{H}^+] = 3.6 \times 10^{-9}M$

b. $[\text{OH}^-] = 6.5 \times 10^{-4}M$

d. $[\text{H}^+] = 0.025M$

Calculating ion concentrations from pH Suppose the pH of a solution is 3.50 and you must determine the concentrations of H^+ and OH^- . The definition of pH relates pH and H^+ ion concentration and can be solved for $[\text{H}^+]$.

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



The pH paper shows that this common cleaner containing ammonia has a pH greater than 11.

Practice!

For more practice calculating pH and pOH from $[\text{OH}^-]$, go to **Supplemental Practice Problems** in Appendix A.

First you need to multiply both sides of the equation by -1 .

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

To calculate $[\text{H}^+]$ using this equation you must take the antilog of both sides of the equation.

$$\text{antilog} (-\text{pH}) = [\text{H}^+]$$

To calculate $[\text{H}^+]$, substitute 3.50 for pH in the equation.

$$\text{antilog} (-3.50) = [\text{H}^+]$$

Use a log table or your calculator to determine the antilog of -3.50 . The antilog is 3.2×10^{-4} .

$$[\text{H}^+] = 3.2 \times 10^{-4} \text{ mol/L}$$

You can calculate $[\text{OH}^-]$ using the relationship $[\text{OH}^-] = \text{antilog} (-\text{pOH})$.

EXAMPLE PROBLEM 19-4

Calculating $[\text{H}^+]$ and $[\text{OH}^-]$ from pH

What are $[\text{H}^+]$ and $[\text{OH}^-]$ in a healthy person's blood that has a pH of 7.40? Assume that the temperature is 298 K.

1. Analyze the Problem

You have been given the pH of a solution and must calculate $[\text{H}^+]$ and $[\text{OH}^-]$. You can obtain $[\text{H}^+]$ using the equation that defines pH. Then, subtract the pH from 14.00 to obtain pOH. The pH is close to 7 but greater than 7, so $[\text{H}^+]$ should be slightly less than 10^{-7} and $[\text{OH}^-]$ should be greater than 10^{-7} .

Known	Unknown
pH = 7.40	$[\text{H}^+] = ? \text{ mol/L}$
	$[\text{OH}^-] = ? \text{ mol/L}$

2. Solve for the Unknown

Write the equation that defines pH and solve for $[\text{H}^+]$.

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

$$[\text{H}^+] = \text{antilog} (-\text{pH})$$

Substitute the known value of pH.

$$[\text{H}^+] = \text{antilog} (-7.40)$$

Use a log table or your calculator to find the antilog. The antilog of -7.40 is 4.0×10^{-8} .

$$[\text{H}^+] = 4.0 \times 10^{-8}M$$

The concentration of hydrogen ion in blood is $4.0 \times 10^{-8}M$.

To determine $[\text{OH}^-]$, calculate pOH using the equation $\text{pH} + \text{pOH} = 14.00$.

Solve for pOH by subtracting pH from both sides of the equation.

$$\text{pOH} = 14.00 - \text{pH}$$

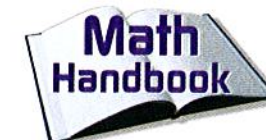
Substitute the known value of pH.

$$\text{pOH} = 14.00 - 7.40 = 6.60$$

Substitute 6.60 for pOH in the equation $[\text{OH}^-] = \text{antilog} (-\text{pOH})$

$$[\text{OH}^-] = \text{antilog} (-6.60)$$

Continued on next page



Review antilogs in the Math Handbook on page 916 of this text.



Blood banks collect blood from healthy people to hold in reserve for persons who need transfusions.

Use a log table or your calculator to find the antilog. The antilog of -6.60 is 2.5×10^{-7} .

$$[\text{OH}^-] = 2.5 \times 10^{-7} \text{M}$$

The concentration of hydroxide ion in blood is $2.5 \times 10^{-7} \text{M}$.

3. Evaluate the Answer

The concentrations of the hydrogen ion and hydroxide ion are correctly stated with two significant figures because the given pH has two decimal places. As predicted, $[\text{H}^+]$ is less than 10^{-7} and $[\text{OH}^-]$ is greater than 10^{-7} .

PRACTICE PROBLEMS

21. The pH is given for three solutions. Calculate $[\text{H}^+]$ and $[\text{OH}^-]$ in each solution.

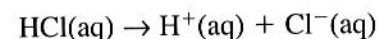
a. pH = 2.37

c. pH = 6.50

b. pH = 11.05

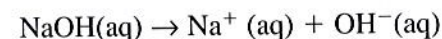
Calculating the pH of solutions of strong acids and strong bases

Look at the bottles of acid and base solutions in **Figure 19-13**. They are labeled with the number of moles of molecules or formula units that were dissolved in a liter of water (M) when the solutions were made. Each of the bottles contains a strong acid or base. Recall from Section 19.2 that strong acids and bases are essentially 100% ionized. That means that this reaction for the ionization of HCl goes to completion.



Every HCl molecule produces one H^+ ion. The bottle labeled $0.1M$ HCl contains 0.1 mole of H^+ ions per liter and 0.1 mole of Cl^- ions per liter. For all strong monoprotic acids, the concentration of the acid is the concentration of H^+ ion. Thus, you can use the concentration of the acid for calculating pH.

Similarly, the $0.1M$ solution of the strong base NaOH in **Figure 19-13** is fully ionized.



One formula unit of NaOH produces one OH^- ion. Thus, the concentration of the hydroxide ion is the same as the concentration of the solution, $0.1M$.

Some strong bases contain two or more hydroxide ions in each formula unit. Calcium hydroxide ($\text{Ca}(\text{OH})_2$) is an example. The concentration of hydroxide ion in a solution of $\text{Ca}(\text{OH})_2$ is twice the concentration of the ionic compound. Thus, the concentration of OH^- in a $7.5 \times 10^{-4}M$ solution of $\text{Ca}(\text{OH})_2$ is $7.5 \times 10^{-4}M \times 2 = 1.5 \times 10^{-3}M$.

PRACTICE PROBLEMS

22. Calculate the pH of the following solutions.

a. $1.0M$ HI

c. $1.0M$ KOH

b. $0.050M$ HNO_3

d. $2.4 \times 10^{-5}M$ $\text{Mg}(\text{OH})_2$

Using pH to calculate K_a Suppose you measured the pH of a $0.100M$ solution of the weak acid HF and found it to be 3.20. Would you have enough information to calculate K_a for HF?



$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

From the pH, you could calculate $[\text{H}^+]$. Then, remember that for every mole per liter of H^+ ion there must be an equal concentration of F^- ion. That means that you know two of the variables in the K_a expression. What about the third, $[\text{HF}]$? The concentration of HF at equilibrium is equal to the initial concentration of the acid ($0.100M$) minus the moles per liter of HF that dissociated ($[\text{H}^+]$). Example Problem 19-5 illustrates a similar calculation for formic acid.

EXAMPLE PROBLEM 19-5

Calculating K_a from pH

The pH of a $0.100M$ solution of formic acid is 2.38. What is K_a for HCOOH?

1. Analyze the Problem

You are given the pH of the solution which allows you to calculate the concentration of the hydrogen ion. You know that the concentration of HCOO^- equals the concentration of H^+ . The concentration of un-ionized HCOOH is the difference between the initial concentration of the acid and $[\text{H}^+]$.

Known

pH = 2.38

concentration of the solution = $0.100M$

Unknown

$K_a = ?$

2. Solve for the Unknown

Write the acid ionization constant expression.

$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

Use the pH to calculate $[\text{H}^+]$.

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

$$[\text{H}^+] = \text{antilog}(-\text{pH})$$

Substitute the known value of pH.

$$[\text{H}^+] = \text{antilog}(-2.38)$$

Use a log table or calculator to find the antilog. The antilog of -2.38 is 4.2×10^{-3} .

$$[\text{H}^+] = 4.2 \times 10^{-3}M$$

$$[\text{HCOO}^-] = [\text{H}^+] = 4.2 \times 10^{-3}M$$

$[\text{HCOOH}]$ equals the initial concentration minus $[\text{H}^+]$.

$$[\text{HCOOH}] = 0.100M - 4.2 \times 10^{-3}M = 0.096M$$

Substitute the known values into the K_a expression.

$$K_a = \frac{(4.2 \times 10^{-3})(4.2 \times 10^{-3})}{(0.096)} = 1.8 \times 10^{-4}$$

The acid ionization constant for HCOOH is 1.8×10^{-4} .

Continued on next page

Practice!

For more practice calculating $[\text{H}^+]$ and $[\text{OH}^-]$ from pH, go to **Supplemental Practice Problems** in Appendix A.



Figure 19-13

The label on a bottle of a strong acid or a strong base tells you immediately the concentration of hydrogen ions or hydroxide ions in the solution. That's because, in solution, strong acids and bases exist entirely as ions. What is $[\text{H}^+]$ in $0.1M$ HCl? What is $[\text{OH}^-]$ in $0.1M$ NaOH?



Natural rubber is an important agricultural export in Southeast Asia. Formic acid is used during the process that converts the milky latex fluid tapped from rubber trees into natural rubber.