

Autoionization and pH Calculations

Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+ , and the hydroxide ion, OH^- when it undergoes autoionization: $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$. The ion product of water, K_w is the equilibrium constant for the autoionization reaction: $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C. Concentrations of hydronium and hydroxide ions in aqueous media are often represented as logarithmic pH and pOH values, respectively. At 25°C, the autoprotolysis equilibrium for water requires the sum of pH and pOH to equal 14 for any aqueous solution. The relative concentrations of hydronium and hydroxide ion in a solution define its status as acidic ($[H_3O^+] > [OH^-]$), basic ($[H_3O^+] < [OH^-]$), or neutral ($[H_3O^+] = [OH^-]$). At 25°C, a pH < 7 indicates an acidic solution, a pH > 7 a basic solution, and a pH = 7 a neutral solution.

22.1 pH and pOH

Learning Objectives

By the end of this section, you will be able to:

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH

The process in which like molecules react to yield ions is called autoionization. Liquid water undergoes autoionization to a very slight extent; at 25 °C, approximately two out of every billion water molecules are ionized. The extent of the water autoionization process is reflected in the value of its equilibrium constant, the ion-product constant for water, K_w :



The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14} . The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium

ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is about 5.6×10^{-13} , roughly 50 times larger than the value at 25 °C.

EXAMPLE 22.1.1

The Inverse Relation between $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$

A solution of an acid in water has a hydronium ion concentration of $2.0 \times 10^{-6} \text{ M}$. What is the concentration of hydroxide ion at 25 °C?

Solution

Use the value of the ion-product constant for water at 25 °C



to calculate the missing equilibrium concentration.

Rearrangement of the K_w expression shows that $[\text{OH}^-]$ is inversely proportional to $[\text{H}_3\text{O}^+]$:

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

Compared with pure water, a solution of acid exhibits a higher concentration of hydronium ions (due to ionization of the acid) and a proportionally lower concentration of hydroxide ions. This may be explained via Le Châtelier's principle as a left shift in the water autoionization equilibrium resulting from the stress of increased hydronium ion concentration.

Substituting the ion concentrations into the K_w expression confirms this calculation, resulting in the expected value:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Check Your Learning

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

✓ Answer

$$[\text{H}_3\text{O}^+] = 1$$

×

$$10^{-11} \text{ M}$$

Hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities that may span many orders of magnitude is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$pX = -\log X$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$pH = -\log[H_3O^+]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[H_3O^+] = 10^{-pH}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

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

or

$$[OH^-] = 10^{-pOH}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_w = [H_3O^+][OH^-]$$

$$-\log K_w = -\log([H_3O^+][OH^-]) = -\log[H_3O^+] + -\log[OH^-]$$

$$pK_w = pH + pOH$$

At 25 °C, the value of K_w is 1.0×10^{-14} , and so:

$$14.00 = pH + pOH$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7} M$ at $25^\circ C$. The pH and pOH of a neutral solution at this temperature are therefore:

$$pH = -\log[H_3O^+] = -\log(1.0 \times 10^{-7}) = 7.00$$

$$pOH = -\log[OH^-] = -\log(1.0 \times 10^{-7}) = 7.00$$

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7} M$ and hydroxide ion molarities less than $1.0 \times 10^{-7} M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7} M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7} M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than $25^\circ C$. For example, the hydronium molarity of pure water at $80^\circ C$ is $4.9 \times 10^{-7} M$, which corresponds to pH and pOH values of:

$$pH = -\log[H_3O^+] = -\log(4.9 \times 10^{-7}) = 6.31$$

$$pOH = -\log[OH^-] = -\log(4.9 \times 10^{-7}) = 6.31$$

At this temperature, then, neutral solutions exhibit $pH = pOH = 6.31$, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at other temperatures, such as enzyme reactions in warm-blooded organisms at a temperature around $36\text{--}40^\circ C$. Unless otherwise noted, references to pH values are presumed to be those at $25^\circ C$ ([Table 22.1](#)).

Table 22.1

Summary of Relations for Acidic, Basic and Neutral Solutions

| Classification | Relative Ion Concentrations | pH at $25^\circ C$ |
|----------------|-----------------------------|--------------------|
| acidic | $[H_3O^+] > [OH^-]$ | $pH < 7$ |
| neutral | $[H_3O^+] = [OH^-]$ | $pH = 7$ |
| basic | $[H_3O^+] < [OH^-]$ | $pH > 7$ |

[Figure 22.1](#) shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH for solutions classified as acidic, basic, and neutral.

Figure 22.2

The pH and pOH scales represent concentrations of H_3O^+ and OH^- , respectively. The pH and pOH values of some common substances at $25^\circ C$ are shown in this chart.

| $[H_3O^+]$ (M) | $[OH^-]$ (M) | pH | pOH | Sample Solution |
|----------------|--------------|----|-----|---|
| 10^1 | 10^{-15} | -1 | 15 | |
| 10^0 or 1 | 10^{-14} | 0 | 14 | ← 1 M HCl acidic |
| 10^{-1} | 10^{-13} | 1 | 13 | |
| 10^{-2} | 10^{-12} | 2 | 12 | ← gastric juice ← lime juice |
| 10^{-3} | 10^{-11} | 3 | 11 | ← 1 M CH_3CO_2H (vinegar) ← stomach acid |
| 10^{-4} | 10^{-10} | 4 | 10 | ← wine ← orange juice |
| 10^{-5} | 10^{-9} | 5 | 9 | ← coffee |
| 10^{-6} | 10^{-8} | 6 | 8 | ← rain water |
| 10^{-7} | 10^{-7} | 7 | 7 | ← pure water neutral |
| 10^{-8} | 10^{-6} | 8 | 6 | ← blood ← ocean water ← baking soda |
| 10^{-9} | 10^{-5} | 9 | 5 | |
| 10^{-10} | 10^{-4} | 10 | 4 | ← Milk of Magnesia |
| 10^{-11} | 10^{-3} | 11 | 3 | |
| 10^{-12} | 10^{-2} | 12 | 2 | ← household ammonia, NH_3 ← bleach |
| 10^{-13} | 10^{-1} | 13 | 1 | |
| 10^{-14} | 10^0 or 1 | 14 | 0 | ← 1 M NaOH basic |
| 10^{-15} | 10^1 | 15 | -1 | |

EXAMPLE 22.1.2

Calculation of pH from $[\text{H}_3\text{O}^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3} \text{ M}$?

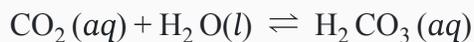
Solution

$$\begin{aligned}\text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92\end{aligned}$$

(The use of logarithms is explained in [Appendix B](#). When taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.)

Check Your Learning

Water exposed to air contains carbonic acid, H_2CO_3 , due to the reaction between carbon dioxide and water:



Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of $2.0 \times 10^{-6} \text{ M}$, about 20-times larger than that of pure water. Calculate the pH of the solution at 25°C .

✓ Answer

5.70

EXAMPLE 22.1.3

Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

Solution

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 7.3$$

$$\log[\text{H}_3\text{O}^+] = -7.3$$

$$[\text{H}_3\text{O}^+] = 10^{-7.3} \text{ or } [\text{H}_3\text{O}^+] = \text{antilog of } -7.3$$

$$[\text{H}_3\text{O}^+] = 5 \times 10^{-8} \text{ M}$$

(On a calculator take the antilog, or the "inverse" log, of -7.3 , or calculate $10^{-7.3}$.)

Check Your Learning

Calculate the hydronium ion concentration of a solution with a pH of -1.07 .

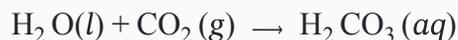
✓ Answer

12 M

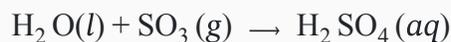
22.1.4 HOW SCIENCES INTERCONNECT

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:



Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2 , SO_2 , SO_3 , NO , and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:



Carbon dioxide is naturally present in the atmosphere because most organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also originates from burning fossil fuels, which have traces of sulfur, and from the process of “roasting” ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 22.2). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

For further information on acid rain, visit this [website](#) hosted by the US Environmental Protection Agency.

Figure 22.3

(a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil.
(b) It also corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by “Eden, Janine and Jim”/Flickr)



(a)



(b)

EXAMPLE 22.1.5

Calculation of pOH

What are the pOH and the pH of a 0.0125-*M* solution of potassium hydroxide, KOH?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[\text{OH}^-] = 0.0125 \text{ M}$:

$$\begin{aligned}\text{pOH} &= -\log[\text{OH}^-] = -\log 0.0125 \\ &= -(-1.903) = 1.903\end{aligned}$$

The pH can be found from the pOH:

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

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.903 = 12.10$$

Check Your Learning

The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3} \text{ M}$. What are the corresponding values of pOH and pH?

✓ Answer

$$\text{pOH} = 11.6, \text{pH} = 2.4$$

22.1.6 Introduction to pH Calculations

$1.0 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$
 $14 = \text{pH} + \text{pOH}$

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

$10^{-\text{pH}}$
 $10^{-\text{pOH}}$

[Watch on YouTube](#)

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter ([Figure 23.3](#)).

Figure 22.4

(a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of \$1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)



(a)



(b)

The pH of a solution may also be visually estimated using colored indicators (Figure 22.4). The acid-base equilibria that enable use of these indicator dyes for pH measurements are described in a later section of this chapter.

Figure 22.5

(a) A solution containing a dye mixture, called universal indicator, takes on different colors depending upon its pH. (b) Convenient test strips, called pH paper, contain embedded indicator dyes that yield pH-dependent color changes on contact with aqueous solutions. (credit: modification of work by Sahar Atwa)



(a)



(b)

Files

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