14.2: pH and pOH

Learning Objectives

- 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

As discussed earlier, 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, the values of which 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:

$$\mathrm{pX} = -\log \mathrm{X} \tag{14.2.1}$$

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

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{14.2.2}$$

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

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{14.2.3}$$

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

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] \tag{14.2.4}$$

or

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}} \tag{14.2.5}$$

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

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{14.2.6}$$

$$-\log K_\mathrm{w} = -\log([\mathrm{H_3O^+}][\mathrm{OH^-}]) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH^-}] \tag{14.2.7}$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} \tag{14.2.8}$$

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

$$14.00 = \mathrm{pH} + \mathrm{pOH} \tag{14.2.9}$$

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

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{14.2.10}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{14.2.11}$$

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).

When $pH = 7$ Solutions are not Neutral

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 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9 × 10^{-7} M, which corresponds to pH and pOH values of:

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

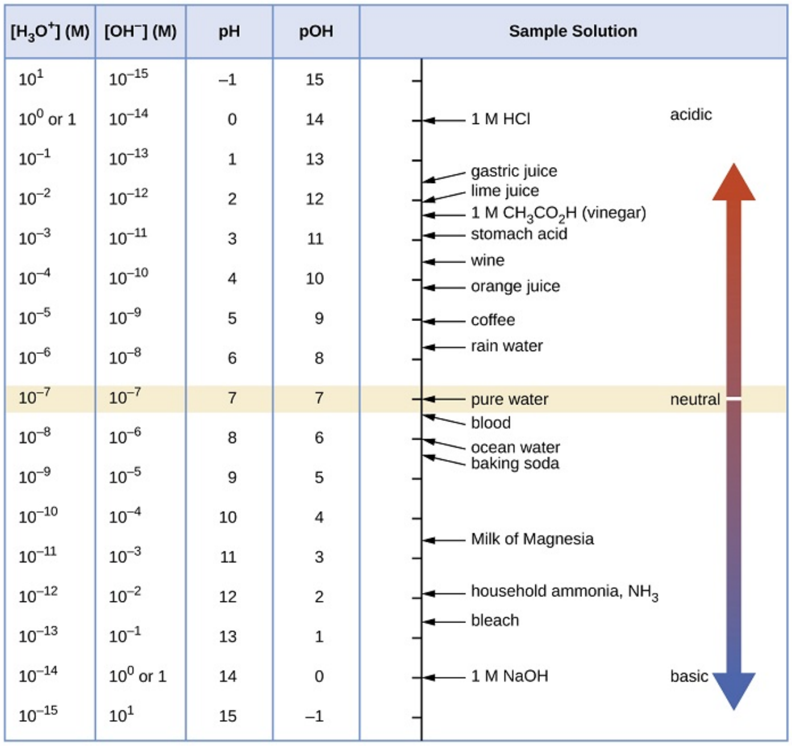
$$\begin{aligned} pOH &= -\log[OH^-] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

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 nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table 14.2.1).

Table 14.2.1: Summary of Relations for Acidic, Basic and Neutral Solutions

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

Figure 14.2.1 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.



$[H_3O^+]$ (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	gastric juice
10^{-2}	10^{-12}	2	12	lime juice; 1 M CH_3CO_2H (vinegar)
10^{-3}	10^{-11}	3	11	stomach acid; wine
10^{-4}	10^{-10}	4	10	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; blood
10^{-8}	10^{-6}	8	6	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	

Figure 14.2.1: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

A table is provided with 5 columns. The first column is labeled “left bracket H subscript 3 O superscript plus right bracket (M).” Powers of ten are listed in the column beginning at 10 superscript 1, including 10 superscript 0 or 1, 10 superscript negative 1, decreasing by single powers of 10 to 10 superscript negative 15. The second column is labeled “left bracket O H superscript negative right bracket (M).” Powers of ten are listed in the column beginning at 10 superscript negative 15, increasing by single powers of 10 to including 10 superscript 0 or 1, and 10 superscript 1. The third column is labeled “p H.” Values listed in this column are integers beginning at negative 1, increasing by ones up to 14. The fourth column is labeled “p O H.” Values in this column are integers beginning at 15, decreasing by ones up to negative 1. The fifth column is labeled “Sample Solution.” A vertical line at the left of the column has tick marks corresponding to each p H level in the table. Substances are listed next to this line segment with line segments connecting them to the line to show approximate p H and p O H values. 1 M H C l is listed at a p H of 0. Gastric juices are listed at a p H of about 1.5. Lime juice is listed at a p H of about 2, followed by 1 M C H subscript 3 C O subscript 2 H, followed by stomach acid at a p H value of nearly 3. Wine is listed around 3.5. Coffee is listed just past 5. Pure water is listed at a p H of 7. Pure blood is just beyond 7. Milk of Magnesia is listed just past a p H of 10.5. Household ammonia is listed just before a pH of 12. 1 M N a O H is listed at a p H of 0. To the right of this labeled arrow is an arrow that points up and down through the height of the column. A beige strip passes through the table and to this double headed arrow at p H 7. To the left of the double headed arrow in this beige strip is the label “neutral.” A narrow beige strip runs through the arrow. Just above and below this region, the arrow is purple. It gradually turns to a bright red as it extends upward. At the top of the arrow, near the head of the arrow is the label “acidic.” Similarly, the lower region changes color from purple to blue moving to the bottom of the column. The head at this end of the arrow is labeled “basic.”

✓ Example 14.2.1: Calculation of pH from $[H_3O^+]$

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

Solution

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) \\ &= 2.92 \end{aligned}$$

Exercise 14.2.1

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

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

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

Answer

5.70

Example 14.2.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Solution

$$pH = -\log[H_3O^+] = 7.3$$

$$\log[H_3O^+] = -7.3$$

$$[H_3O^+] = 10^{-7.3}$$

or

$$[H_3O^+] = \text{antilog of} -7.3$$

$$[H_3O^+] = 5 \times 10^{-8}\ M$$

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

Exercise 14.2.2

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

Answer

12 M

14.2.1: Environmental Science

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

$$H_2O(l) + CO_2(g) \longrightarrow H_2CO_3(aq) \tag{14.2.12}$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{14.2.13}$$

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:

$$H_2O(l) + SO_3(g) \longrightarrow H_2SO_4(aq) \tag{14.2.14}$$

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \tag{14.2.15}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems 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 14.2.2). 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.

(a) (b)

Figure 14.2.2: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is 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)

Two photos are shown. Photograph a on the left shows the upper portion of trees against a bright blue sky. The tops of several trees at the center of the photograph have bare branches and appear to be dead. Image b shows a statue of a man that appears to from the revolutionary war era in either marble or limestone.

✓ Example 14.2.3: 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 $[OH^-]$ = 0.0125 M:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log 0.0125$$

$$= -(-1.903) = 1.903$$

The pH can be found from the pOH:

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

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

? Exercise 14.2.3

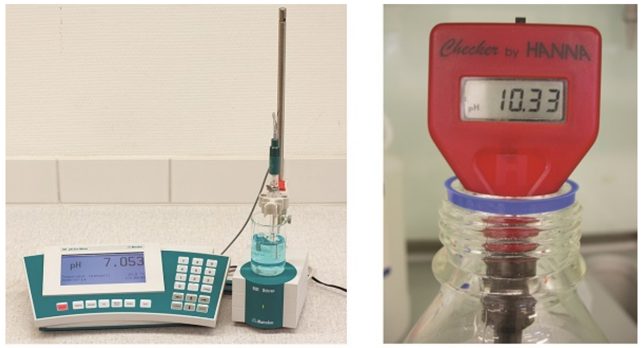
The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3}\ M$. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6,

pH = 14.00 - pOH = 2.4

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 14.2.3).



(a) (b)

Figure 14.2.3: (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)

This figure contains two images. The first, image a, is of an analytical digital p H meter on a laboratory counter. The second, image b, is of a portable hand held digital p H meter.

The pH of a solution may also be visually estimated using colored indicators (Figure 14.2.3).

(a) (b)

Figure 14.2.4: (a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-M solutions of progressively weaker acids: HCl (pH = l), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa).

This figure contains two images. The first shows a variety of colors of solutions in labeled beakers. A red solution in a beaker is labeled "0.10 M H C l." An orange solution is labeled "0.10 M C H subscript 3 C O O H." A yellow-orange solution is labeled "0.1 M N H subscript 4 C l." A yellow solution is labeled "deionized water." A second solution beaker is labeled "0.10 M K C l." A green solution is labeled "0.10 M aniline." A blue solution is labeled "0.10 M N H subscript 4 C l (a q)." A final beaker containing a dark blue solution is labeled "0.10 M N a O H." Image b shows pHydrion paper that is used for measuring pH in the range of p H from 1 to 12. The color scale for identifying p H based on color is shown along with several of the test strips used to evaluate p H.

Summary

The concentration of hydronium ion in a solution of an acid in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $\mathrm{pH} = -\log \mathrm{H_3O^+}$. The concentration of OH^- can be expressed as the pOH of the solution: $\mathrm{pOH} = -\log[\mathrm{OH^-}]$. In pure water, pH = 7.00 and pOH = 7.00

14.2.2: Key Equations

- $\mathrm{pH} = -\log[\mathrm{H_3O^+}]$
- $\mathrm{pOH} = -\log[\mathrm{OH^-}]$
- $[H_3O^+] = 10^{-\mathrm{pH}}$
- $[OH^-] = 10^{-\mathrm{pOH}}$
- pH + pOH = $\mathrm{p}K_\mathrm{w}$ = 14.00 at 25 °C

Glossary

acidic

describes a solution in which $[H_3O^+] > [OH^-]$

basic

describes a solution in which $[H_3O^+] < [OH^-]$

neutral

describes a solution in which $[H_3O^+] = [OH^-]$

pH

logarithmic measure of the concentration of hydronium ions in a solution

pOH

logarithmic measure of the concentration of hydroxide ions in a solution

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