The Self-Ionization of Water

• Water is both an acid and a base. This means that a water molecule can either give or receive a proton.

\[ \text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \leftrightarrow \text{H}_3\text{O}^+(aq) + \text{OH}^- (aq) \]

base acid

• A pair of water molecules are in equilibrium with two ions—a hydronium ion and a hydroxide ion—in a reaction known as the **self-ionization of water**.
The Self-Ionization of Water, continued

- In pure water, the two ions must share the same concentration.

- Experiments show that this concentration is $1.00 \times 10^{-7}$ M at 25°C.

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ M}$$
The Self-Ionization of Water, *continued*

\[ \text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \]

- Water molecule
- Water molecule
- Hydronium ion
- Hydroxide ion
The Self-Ionization of Water, continued

The Self-Ionization Constant of Water

• An equilibrium-constant expression relates the concentrations of species involved in an equilibrium.

• The relationship for the water equilibrium is simply \([\text{H}_3\text{O}^+][\text{OH}^-] = K_{eq}\).

• This equilibrium constant, called the self-ionization constant is so important that it has a special symbol, \(K_w\).
The value of $K_w$ can be found from the known concentrations of the hydronium and hydroxide ions in pure water.

$$[H_3O^+][OH^-] = K_w = (1.00 \times 10^{-7})(1.00 \times 10^{-7}) = 1.00 \times 10^{-14}$$

The product of these two ion concentrations is always a constant.

- Anything that increases one of the ion concentrations decreases the other.
- If you know one of the ion concentrations, you can calculate the other.
The concentration of hydronium ions in a solution expresses its **acidity**.

The concentration of hydroxide ions in a solution expresses its **basicity**.
When the concentration of $\text{H}_3\text{O}^+$ goes up, the concentration of $\text{OH}^-$ goes down, and vice versa.

- **Acidic solution**
  \[ [\text{H}_3\text{O}^+] > 10^{-7} \text{ M} > [\text{OH}^-] \]

- **Neutral solution**
  \[ [\text{H}_3\text{O}^+] = 10^{-7} \text{ M} = [\text{OH}^-] \]

- **Basic solution**
  \[ [\text{H}_3\text{O}^+] < 10^{-7} \text{ M} < [\text{OH}^-] \]
### The Self-Ionization of Water, *continued*

#### The Self-Ionization Constant of Water, *continued*

<table>
<thead>
<tr>
<th>Solution</th>
<th>$[\text{H}_3\text{O}^+]$ (M)</th>
<th>$[\text{OH}^-]$ (M)</th>
<th>$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>$1.0 \times 10^{-7}$</td>
<td>$1.0 \times 10^{-7}$</td>
<td>$1.0 \times 10^{-14}$</td>
</tr>
<tr>
<td>0.10 M strong acid</td>
<td>$1.0 \times 10^{-1}$</td>
<td>$1.0 \times 10^{-13}$</td>
<td>$1.0 \times 10^{-14}$</td>
</tr>
<tr>
<td>0.010 M strong acid</td>
<td>$1.0 \times 10^{-2}$</td>
<td>$1.0 \times 10^{-12}$</td>
<td>$1.0 \times 10^{-14}$</td>
</tr>
<tr>
<td>0.10 M strong base</td>
<td>$1.0 \times 10^{-13}$</td>
<td>$1.0 \times 10^{-1}$</td>
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</tr>
<tr>
<td>0.010 M strong base</td>
<td>$1.0 \times 10^{-12}$</td>
<td>$1.0 \times 10^{-2}$</td>
<td>$1.0 \times 10^{-14}$</td>
</tr>
<tr>
<td>0.025 M strong acid</td>
<td>$2.5 \times 10^{-2}$</td>
<td>$4.0 \times 10^{-13}$</td>
<td>$1.0 \times 10^{-14}$</td>
</tr>
<tr>
<td>0.025 M strong base</td>
<td>$4.0 \times 10^{-13}$</td>
<td>$2.5 \times 10^{-2}$</td>
<td>$1.0 \times 10^{-14}$</td>
</tr>
</tbody>
</table>
Determining $[\text{OH}^-]$ or $[\text{H}_3\text{O}^+]$ Using $K_w$

Sample Problem A

What is $[\text{OH}^-]$ in a $3.00 \times 10^{-5}$ M solution of HCl?
Determining $[\text{OH}^-]$ or $[\text{H}_3\text{O}^+]$ Using $K_w$, continued

Sample Problem A Solution

$[\text{H}_3\text{O}^+] = 3.00 \times 10^{-5} \text{ M}$

$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$

$K_w = 1.00 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-] = (3.00 \times 10^{-5})[\text{OH}^-]$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-14}}{3.00 \times 10^{-5}} = 3.33 \times 10^{-10} \text{ M}$$
The Meaning of pH

pH and Acidity

• When acidity and basicity are exactly balanced such that the numbers of $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ions are equal, we say that the solution is neutral.

• Pure water is neutral because it contains equal amounts of the two ions.
The Meaning of pH, continued

pH and Acidity, continued

• A solution made by dissolving 0.100 mol of NaOH in 1.00 L of water has a hydroxide ion concentration of 0.100 M.

• The hydronium ion concentration can be calculated using $K_w$.

$$\left[\text{H}_3\text{O}^+\right] = \frac{\left[\text{H}_3\text{O}^+\right]\left[\text{OH}^-\right]}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.100} = 1.00 \times 10^{-13}$$
In 1909, Danish chemist Søren Sørensen proposed using the negative of the power of 10 (that is, the negative logarithm) of \([H_3O^+]\) as the index of basicity and acidity.

He called this measure the **pH**. The letters *p* and *H* represent *p*ower of *H*ydrogen.

pH can be calculated by the following mathematical equation:

\[
pH = -\log [H_3O^+]
\]
The Meaning of pH, continued
Calculating pH from $[H_3O^+]$

• Because of the negative sign, as the hydronium ion concentration increases, the pH will *decrease*.

  • A solution of pH 0 is very acidic.

  • A solution of pH 14 is very alkaline.

  • A solution of pH 7 is neutral.
The Meaning of pH, continued
Calculating pH from \([H_3O^+]\), continued

- The pH equation may be rearranged to calculate the hydronium ion concentration from the pH.

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

- Because pH is related to powers of 10, a change in one pH unit corresponds to a tenfold change in the concentrations of the hydroxide and hydronium ions.
pH Values of Some Common Materials

Battery acid | Stomach acid | Apple juice | Black coffee | Pure water | Antacid | Baking soda | Hand soap | Household ammonia | Drain cleaner

more acidic | NEUTRAL | more basic
Calculating pH for an Acidic or Basic Solution

Sample Problem B
What is the pH of (a) a 0.000 10 M solution of HNO₃, a strong acid, and (b) a 0.0136 M solution of KOH, a strong base?
Calculating pH for an Acidic or Basic Solution, *continued*

Sample Problem B Solution

(a) Concentration of HNO$_3$ solution = 0.000 10 M = $1.0 \times 10^{-4}$ M; pH = ?

(b) Concentration of KOH solution = 0.0136 M = $1.36 \times 10^{-2}$ M; pH = ?

$K_w = 1.00 \times 10^{-14}$
Calculating pH for an Acidic or Basic Solution, continued
Sample Problem B Solution

(a) \[ \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.0 \times 10^{-4}) = -(-4.00) = 4.00 \]

(b) \[ [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{1.36 \times 10^{-2}} = 7.53 \times 10^{-13} \]

\[ \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.35 \times 10^{-13}) = -(-12.13) = 12.13 \]
Calculating \([H_3O^+]\) and \([OH^-]\) from pH

Sample Problem C

What are the concentrations of the hydronium and hydroxide ions in a sample of rain that has a pH of 5.05?
Calculating $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ from pH, continued

Sample Problem C Solution

pH = 5.05

$K_w = 1.00 \times 10^{-14}$

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

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

(a) $[\text{H}_3\text{O}^+] = 10^{-pH} = 10^{-5.05} = \boxed{8.9 \times 10^{-6} \text{ M}}$

(b) $[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.00 \times 10^{-14}}{8.9 \times 10^{-6}} = \boxed{1.1 \times 10^{-9} \text{ M}}$
Measuring pH

Indicators

- Certain dyes, known as *indicators*, turn different colors in solutions of different pH.

  - An *indicator* is a compound that can reversibly change color depending on the pH of the solution or other chemical change.

- Thymol blue is an example of an indicator.

  - It is yellow in solutions whose pH is between 3 and 8 but blue in solutions whose pH is 10 or higher.
Measuring pH, continued

pH Meters

• A pH meter is an electronic instrument equipped with a probe that can be dipped into a solution.

• The probe has two electrodes, one of which is sensitive to the hydronium ion.

• An electrical voltage develops between the two electrodes, and the circuitry measures this voltage.

• The instrument converts the measurement into a pH reading, which is displayed on the meter’s screen.