

# 1 Learning Objectives

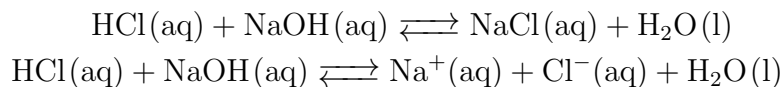
1. How does water act as an acid or a base?
2. What is the relationship between  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$ ?
3. How do we measure the strength of an acid?

# 2 Recap

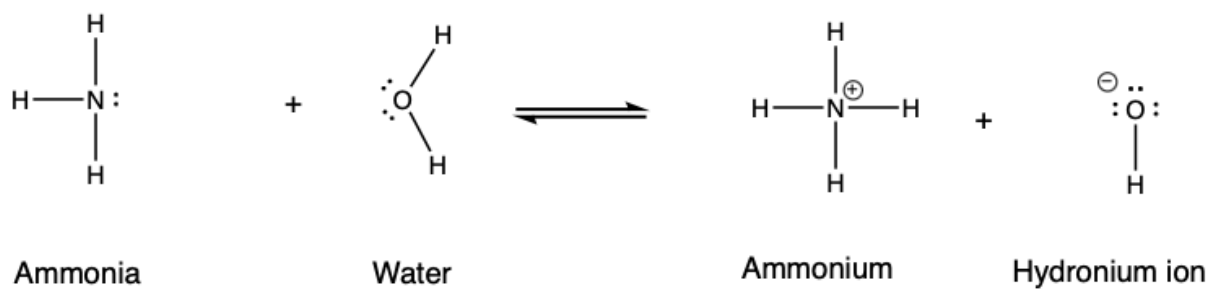
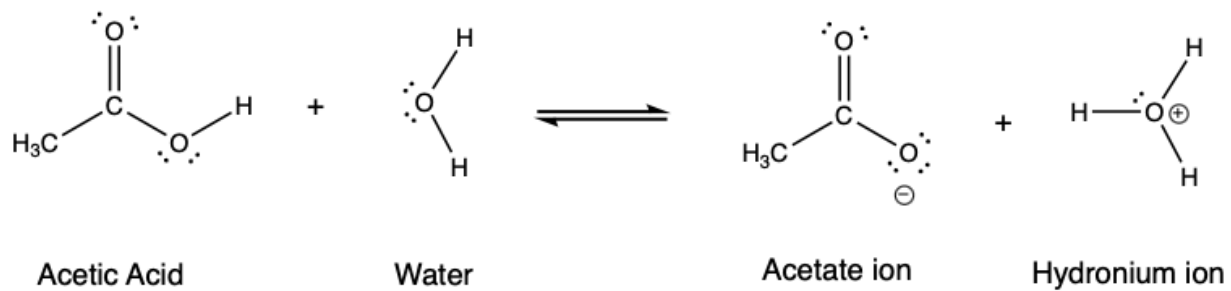
1. Acids and Bases share distinct physical and chemical properties.
  - (a) Touch, taste, reaction with metals, etc.
2. Different theories on how to define if a substance is an acid or base?

Theory	Acid	Base	Notes
Arrhenius			Limited to aqueous solutions
Brønsted			Acids must contain $\text{H}^+$
Lewis			Limited to transfer of a single electron

3. Within the Brønsted definition: we looked at how combining acids and bases create salt and water (neutralization reactions).

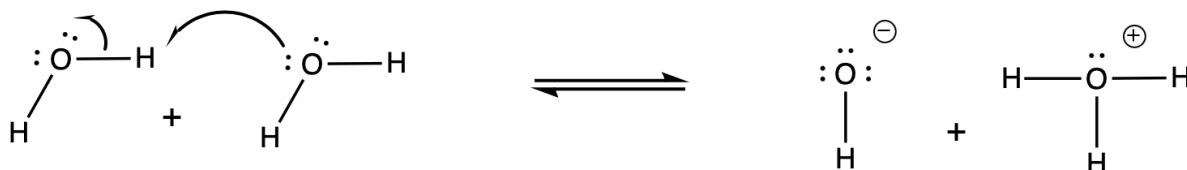


4. Within the Brønsted definition: we looked at determining conjugate acid-base pairs.



### 3 Acid-Base Properties of Aqueous Solutions are Governed by the Autoionization of Water

The previous example shows that water can act as an acid or a base according to the environment around it. On its own, water is a weak electrolyte but does undergo ionization to a small extent (as demonstrated below). This reaction is sometimes known as **autoionization of water**.



The reaction as written indicates that there is an equilibrium between liquid water (reactants) and the hydronium and hydroxide ions (products). Therefore, we can express the equilibrium constant for the autoionization of water:

$$K = \frac{\alpha_{\text{H}_3\text{O}^+} \alpha_{\text{OH}^-}}{\alpha_{\text{H}_2\text{O}}^2} \quad (1)$$

Typically, the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are sufficiently small that their activities are to a good approximation equal to their molar concentrations. This means that  $\alpha_{\text{H}_3\text{O}^+} = [\text{H}_3\text{O}^+]$ ,  $\alpha_{\text{OH}^-} = [\text{OH}^-]$ , and  $\alpha_{\text{H}_2\text{O}} = 1$ . As a result, our equilibrium constant above can be rewritten as:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad (2)$$

or

$$K_w = [\text{H}^+][\text{OH}^-] \quad (3)$$

$K_w$  is known as the **ion-product constant** which is the product of the molar concentrations of  $\text{H}^+$  and  $\text{OH}^-$  ions at a particular temperature. It is important to note that  $K_w$  (like all other equilibrium constants) is dimensionless. The actual expression (in terms of activity) is written as:

$$K_w = \left[ \frac{\text{H}_3\text{O}^+}{c^\circ} \right] \left[ \frac{\text{OH}^-}{c^\circ} \right] \quad (4)$$

where  $c^\circ = 1M$ . For simplicity  $c^\circ$  is omitted from the  $K_w$  expressions. Therefore, it is imperative to be careful to convert the concentration units to  $M$  before using equation 3.

In pure water at  $25^\circ\text{C}$ , the concentration of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are equal and found to be  $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7}M$ . This means that  $K_w$  is:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [1 \times 10^{-7}M][1 \times 10^{-7}M] = 1 \times 10^{-14} \quad (5)$$

The value of  $K_w$  is fixed at 25°C regardless if we have a pure solution of water or an aqueous solution of dissolved species. Now given an arbitrary solution, we can now determine how acidic or basic it is.

### 3.1 Measuring the Acidity or Alkalinity of a Solution

We can determine if a dilute solution is acidic or basic by measuring (or calculating) the relative concentration of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ .

$[\text{H}_3\text{O}^+]$ $[\text{OH}^-]$	Acidic
$[\text{H}_3\text{O}^+]$ $[\text{OH}^-]$	Basic
$[\text{H}_3\text{O}^+]$ $[\text{OH}^-]$	Neutral

In practice, we can change the  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$ , but we cannot vary them independently. If we adjust the solutions  $[\text{H}_3\text{O}^+]$ , the  $[\text{OH}^-]$  *must* change to.

#### 3.1.1 Exercise

The concentration of  $\text{OH}^-$  ions in certain household cleaning solutions is approximately 0.0025M. What is the concentration of  $\text{H}_3\text{O}^+$  ions. Is the solution acidic, basic, or neutral?

### 3.2 pH - a Measure of Acidity

We typically deal with very small concentrations of  $[\text{H}^+]$  and  $[\text{OH}^-]$  ions. A more practical measure of acidity (and alkalinity) is called **pH**. The **pH** of a solution is defined as the *negative logarithm (base 10) of the hydrogen ion activity*:

$$\text{pH} = -\log(\alpha_{\text{H}^+}) \quad \text{or} \quad \text{pH} = -\log(\alpha_{\text{H}_3\text{O}^+}) \quad (6)$$

Similarly as described in the previous section, for dilute solutions in which the hydrogen (and hydronium) ion concentrations can be well approximated by its concentration relative to standard concentration:

$$\text{pH} = -\log(\alpha_{\text{H}^+}) \approx \text{pH} = -\log([\text{H}^+]) \quad (7)$$

Again,  $[\text{H}^+]$  typically has units on  $M$ , however, we ignore units for convenience. The pH of a solution is a dimensionless quantity. The equation above is simply designed to give a convenient number to work with.

Because pH is simply a way to express hydrogen ion concentration, acidic and basic solution can be identified based on their pH.

If a solution is neutral, that is equivalent as saying the concentrations of  $\text{H}_3\text{O}^+ = \text{OH}^-$ . With that, we can calculate the pH of a neutral solution.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_3\text{O}^+]^2$$

$$[\text{H}_3\text{O}^+] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}$$

$$\text{pH} = -\log([\text{H}_3\text{O}^+]) = -\log(1.00 \times 10^{-7}) = 7$$

We can follow similar procedures for acidic solutions and basic solutions. The table below summarizes the conditions of a solution at 25°C.

	$[\text{H}^+]$	pH
Acidic		
Basic		
Neutral		

**3.2.1 Exercise**

The pH of rainwater collected in a region of the northeastern United States on a particular day was 4.82. Calculate the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  concentration of the rainwater.