

# 15. The Relative Strengths of Some Acids

## Introduction

Acids and bases, two closely connected types of substances, are part of our everyday lives. They can be found in foods, soft drinks, medicines, and cleaning products.

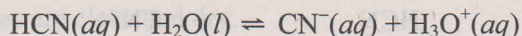
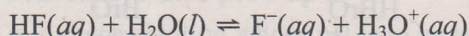
The relationship between acids and bases occurs because these substances react readily with each other. An acid–base reaction is a competition for protons (Ebbing/Gammon, Chapter 15). The extent of the reaction depends on the strengths of the acid and the base. A strong acid reacts with a base more completely than a weaker acid reacts with the same base. This difference enables us to measure the relative strengths of acids (and bases)

## Purpose

You will estimate or measure the pH of various solutions, using indicators, pH paper, and (optionally) a pH meter.

## Relative Strengths of Acids

How can you determine the relative strengths of two acids? As an example, let us consider how you would determine the relative strengths of HF (hydrofluoric acid) and HCN (hydrocyanic acid). You would prepare isomolar aqueous solutions of these acids and examine the extent of their ionizations in water. The equations that describe these reactions are



The ionization of the stronger acid will be greater than the ionization of the weaker acid. As a result, the stronger acid will provide more  $\text{H}_3\text{O}^+$  ions than the weaker acid. You would find in this case that  $[\text{H}_3\text{O}^+]$  is greater in the solution of HF. You would then know that HF is a stronger acid than HCN.

The relative strengths of the acids in Table 15.1 were determined by this method. The table also shows the relative strengths of the conjugate bases of the acids. When you compare the strengths of any two acids in the table, you will note that the stronger acid has the weaker conjugate base.

## Two Special Notes

The aluminum cation,  $\text{Al}^{3+}$ , exists in aqueous solution as the hydrated ion,  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ . Table 15.1 shows that this ion is an acid. Why? The water molecules are bonded to the metal through lone pairs of electrons on the oxygen atoms. The positively charged aluminum ion draws electrons from the oxygen atoms, which, in turn, draw electrons from the O–H bonds and weakens them. As a result, the water molecules tend to be acidic:

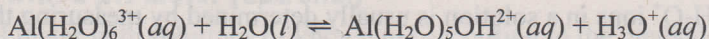
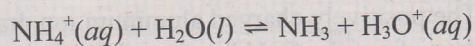


Table 15.1  
Relative Strengths of Some Acids and Bases

Acid		Base	
Strongest acids	HClO <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup>	Weakest bases
	H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	
	HI	I <sup>-</sup>	
	HBr	Br <sup>-</sup>	
	HCl	Cl <sup>-</sup>	
	HNO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	
	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	
	HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	
	H <sub>2</sub> SO <sub>3</sub>	HSO <sub>3</sub> <sup>-</sup>	
	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	
	HNO <sub>2</sub>	NO <sub>2</sub> <sup>-</sup>	
	HF	F <sup>-</sup>	
	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	
	Al(H <sub>2</sub> O) <sub>6</sub> <sup>3+</sup>	Al(H <sub>2</sub> O) <sub>5</sub> OH <sup>2+</sup>	
	H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>	
	H <sub>2</sub> S	HS <sup>-</sup>	
	HClO	ClO <sup>-</sup>	
	HBrO	BrO <sup>-</sup>	
	NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>	
	HCN	CN <sup>-</sup>	
	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	
	H <sub>2</sub> O <sub>2</sub>	HO <sub>2</sub> <sup>-</sup>	
	HS <sup>-</sup>	S <sup>2-</sup>	
Weakest acids	H <sub>2</sub> O	OH <sup>-</sup>	Strongest bases
	NH <sub>3</sub>	NH <sub>2</sub> <sup>-</sup>	
	OH <sup>-</sup>	O <sup>2-</sup>	

You will also note that Table 15.1 indicates that the ammonium ion, NH<sub>4</sub><sup>+</sup>, is an acid. The acidity of this ion is a result of the reaction shown in the following chemical equation:



### pH

The concentration of H<sub>3</sub>O<sup>+</sup> ions in a solution is usually determined by measuring the pH of the solution. The pH is defined as

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

(Ebbing/Gammon, Section 15.8). If the pH of the solution is low, the ionization equilibrium favors the right side of the chemical equation because [H<sub>3</sub>O<sup>+</sup>] is large. However, if the pH is high, the equilibrium

favors the left side because  $[H_3O^+]$  is small. When two acids are compared, the stronger acid yields a solution with the lower pH.

### Concept of the Experiment

You will estimate or measure the pH of isomolar solutions of HCl,  $H_3PO_4$ ,  $HC_2H_3O_2$ ,  $NaH_2PO_4$ ,  $Al(NO_3)_3$ ,  $Zn(NO_3)_2$ , and  $NH_4NO_3$ . Many of these substances can be found in Table 15.1. You will be able to judge the strengths of these acids from the pH values of their solutions. You will also have an opportunity to estimate or measure the pH of several common substances: vinegar, carbonated water, tap water, and distilled water

## Procedure

### Getting Started

1. Obtain 4 large test tubes. Use a graduated cylinder to place 4 mL of distilled water in each test tube. Mark the height of the meniscus in each tube with a marking pencil. Pour out the water and dry the test tubes.
2. Obtain a small (about 1/2-inch) strip of wide-range pH paper for each solution that you will test. Handle these pieces as little as possible. Place them on a clean paper towel.
3. Obtain a small (about 1/2-inch) strip of each narrow-range pH paper that is available. Handle these pieces as little as possible. Place them on a clean paper towel. Mark the pH range for each strip on the paper towel. Replace these strips as needed.
4. If you are going to use a pH meter, obtain instructions for using it.

### Doing the Experiment with Indicators and pH Paper

1. Complete Steps 2 through 6 for each solution whose pH is to be estimated.
2. Make sure your test tubes are clean and dry.
3. Obtain 4 mL of the solution\* to be tested in each of the test tubes.
4. Using a clean, dry stirring rod, place 1 drop of the solution from one of the test tubes on a piece of wide-range pH paper. Do not contaminate the other unused strips. Using the result that you obtain, select the appropriate short-range paper and use it in the same manner. Record your estimate.
5. Use 3 drops of a different indicator solution for each test tube. The indicators are thymol blue, methyl orange, methyl red, and bromthymol blue (see Figure D.1 in Appendix D for the pH range for these indicators).
6. Estimate the pH by comparing your results with Figure D.1. In some instances, you may be able to estimate to the nearest 0.1 pH unit; in other instances, you may be able to estimate only to the nearest 0.5 pH unit. Record your estimate.

\*Note: Instructors, please refer to the IRM for acceptable concentration range for these solutions.

### Measuring the pH with a pH Meter (optional)

1. Calibrate the pH meter with solutions of known pH according to the methods prescribed by your laboratory instructor.
2. Measure, and record to the nearest 0.01 pH unit, the pH of each solution.

Date: \_\_\_\_\_  
Course/Section: \_\_\_\_\_  
Instructor: \_\_\_\_\_

Student name: \_\_\_\_\_  
Team members: \_\_\_\_\_

## The Relative Strengths of Some Acids

### Prelaboratory Assignment

1. Provide definitions for the following terms:

a. Brønsted–Lowry acid

b. Brønsted–Lowry base

c. pH

d. Acidic solution

e. Basic solution

f. Neutral solution

g. Indicator

h. pH paper

i. pH meter

2. a. A solution causes a yellow color with thymol blue, an orange color with methyl orange, a red color with methyl red, and a yellow color with bromthymol blue. The pH must lie between \_\_\_\_\_ and \_\_\_\_\_. The estimated pH is \_\_\_\_\_ ± \_\_\_\_\_.
- b. A solution causes a yellow color with thymol blue, yellow colors with both methyl orange and methyl red, and a green color with bromthymol blue. The pH must lie between \_\_\_\_\_ and \_\_\_\_\_. The estimated pH is \_\_\_\_\_ ± \_\_\_\_\_.

Date: \_\_\_\_\_  
 Course/Section: \_\_\_\_\_  
 Instructor: \_\_\_\_\_

Student name: \_\_\_\_\_  
 Team members: \_\_\_\_\_

## The Relative Strengths of Some Acids

### Results

Solution	pH from pH Paper	pH from Indicators	pH from pH Meter
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_____	_____	_____	_____
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### Purpose

_____	_____	_____	_____
_____	_____	_____	_____

### Concept of the Experiment

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### Procedure

_____	_____	_____	_____
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### Getting Started

_____	_____	_____	_____
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_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

### Questions

- Calculate the concentration of  $H_3O^+$  ions in the most acidic solution that you examined. Use your most precise pH measurement.

- b. Calculate the concentration of  $\text{H}_3\text{O}^+$  ions in the least acidic solution that you examined. Use your most precise pH measurement.
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2. a. Arrange the acids that you used in order of *decreasing* acidity. Use your most precise pH measurements. Exclude the common household substances.
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- b. How does your arrangement compare with the first column in Table 15.1, insofar as a comparison can be made? Comment.
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- c. Comment on the relative acidities of  $\text{H}_3\text{PO}_4$  and the  $\text{H}_2\text{PO}_4^+$  ion.
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3. Give the chemical reactions that show why solutions of  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Zn}(\text{NO}_3)_2$ , and  $\text{NH}_4\text{NO}_3$  have the pH values that you found.
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4. Arrange the common household substances in order of *decreasing* acidity.

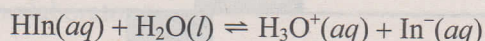
## Appendix D: Indicators, pH Paper, and pH Meters

The pH of a solution can be either estimated, using acid–base indicators or pH paper, or measured directly with a pH meter. Each of these methods will be discussed in turn.

### Indicators

Acid–base indicators (Ebbing/Gammon, Chapter 15) are usually very complicated molecules that are intensely colored. These substances are also weak acids or bases. For that reason, many aspects of the chemistry of these indicators are very similar to those of other weak acids or bases.

Methyl orange, for example, is an acid–base indicator and a weak acid. Because of its complicated nature, we write its formula in abbreviated form as HIn. This substance dissociates partially in solution according to



The color of the acid form of this indicator is red, whereas the color of  $\text{In}^-$  is yellow.

The position of the equilibrium between HIn and  $\text{In}^-$  depends on the pH of the solution to which the indicator has been added. According to Le Châtelier's principle (Ebbing/Gammon, Chapter 14), a large concentration of  $\text{H}_3\text{O}^+$  ions (low pH) will cause the equilibrium to shift almost completely to the left. The color of the solution will then be red, the color of HIn. At lower concentrations of  $\text{H}_3\text{O}^+$  ions (higher pH), the equilibrium will shift from left to right, resulting in various hues of orange. If the equilibrium is shifted almost completely to the right, the color of the solution will be yellow, the color of  $\text{In}^-$ .

It is important to note that because an indicator is intensely colored, only small amounts are required. Because only small amounts are used, the indicator does not measurably alter the pH of the solution to be tested.

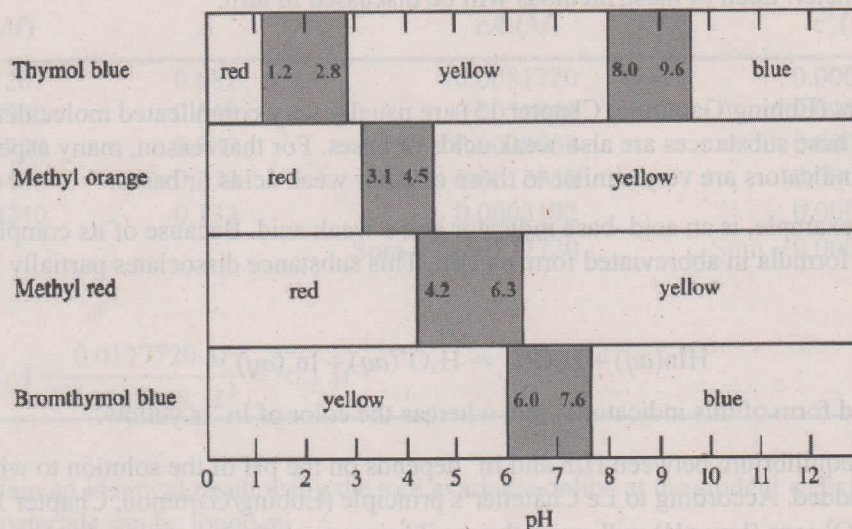
Consider the chart in Figure D.1, which gives the colors of four indicators as a function of pH. Returning to methyl orange, you will see from the chart that a solution containing this indicator will be red if the pH is less than 3.1, orange if the pH lies between 3.1 and 4.5, and yellow if the pH is greater than 4.5. By using all of the indicators given in the chart, you should be able to estimate an unknown pH that lies between 1.2 and 9.6. If the pH does not lie within this range, you will at least be able to say that it is less than 1.2 or greater than 9.6.

Because we must depend on the color of an indicator to estimate the pH, the solution to be tested must be colorless or very nearly colorless. This is one of the principal drawbacks to the use of indicators.



FIGURE D.1

Color changes for four acid–base indicators. Shaded areas indicate the pH intervals in which the colors change.



### pH Paper

Paper strips that have been treated with a mixture of indicators can be used to estimate the pH of a solution. The indicators are chosen such that each one will change color at a different pH. The pH is estimated by moistening the paper with the solution being tested and then matching its color with a color on a chart provided by the manufacturer of the paper. The strips of paper are called *pH paper*. Again, colored solutions cannot be used.

Both wide-range and short-range papers are available. A wide-range paper might cover eight to eleven pH units (say, pH 1 to 11), whereas a short-range paper might cover only two or three pH units (say, pH 1 to 2.5).

### pH Meters

A pH meter and its electrodes form a sensitive electrochemical device that makes possible the accurate, reproducible, and reliable measurement of the pH of a solution. Moreover, the solution does not need to be colorless.

There are several exterior designs for commercial pH meters. Meters may appear to differ from one another because they come from different manufacturers or, if they come from the same manufacturer, because they are different models with different prices. The differences usually lie in the way the measured pH is displayed, the positions of the control knobs, the types of electrodes, and the manner in which these electrodes are held in position.

Any pH meter, no matter how it looks, is just a voltmeter that measures the voltage of an electric current flowing through a solution between two electrodes. There is a direct relationship between the voltage and the pH of the solution (Ebbing/Gammon, Section 19.7). As a result, the meter on the instrument is calibrated directly in pH units rather than in volts.

Two electrodes are required. One of them is called a *glass electrode*. This electrode is sensitive to the concentration of  $\text{H}_3\text{O}^+$  ions in the solution. The other is called the *reference electrode*. Its operation is virtually independent of the composition of the solution. These electrodes are sometimes combined into

a single entity called a *combination electrode*. However, there are really two different electrodes present.

Although the operating rules for a pH meter depend on the model and the manufacturer, there are several steps you will need to follow with any instrument.

1. The electrodes should always be kept in a solution except when you are transferring them from one solution to another. When you transfer them, avoid contaminating the solutions. During the transfer, rinse the electrodes with a stream of distilled water, and catch the water in a beaker. Remove the excess water from the electrodes with tissue paper before you immerse the electrodes in the next solution. Do not touch the electrodes with your hand. Handle them with care because they are fragile.
2. If there is a knob that adjusts the pH meter for different temperatures, it should be set to the temperature of the solution whose pH is to be measured. More often than not, this temperature is also the temperature of the laboratory.
3. The pH meter must be calibrated or standardized with a solution whose pH is known before you can measure an unknown pH with accuracy. These solutions of known pH are called *buffer solutions*.
4. Place your solution in the smallest container that is consistent with the experiment. Under the simplest of circumstances, you can measure the pH of a few milliliters of a solution in a large test tube with a combination electrode or in a 50-mL beaker with two electrodes.
5. You should be able to read the pH of a solution about 10 s after the electrodes have been immersed. The reading should be steady and not abruptly changing. If sudden changes do occur, consult your laboratory instructor. Additional operating rules may be issued by your laboratory instructor.