A. 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 16) 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

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

The color of the acid form of this indicator is red, whereas the color of In^- is yellow.

The position of the equilibrium between HIn and In^- depends on the pH of the solution to which the indicator has been added. According to Le Chatelier's principle (Ebbing/Gammon, Chapter 15), a large concentration of H_3O^+ 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 H_3O^+ 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 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.

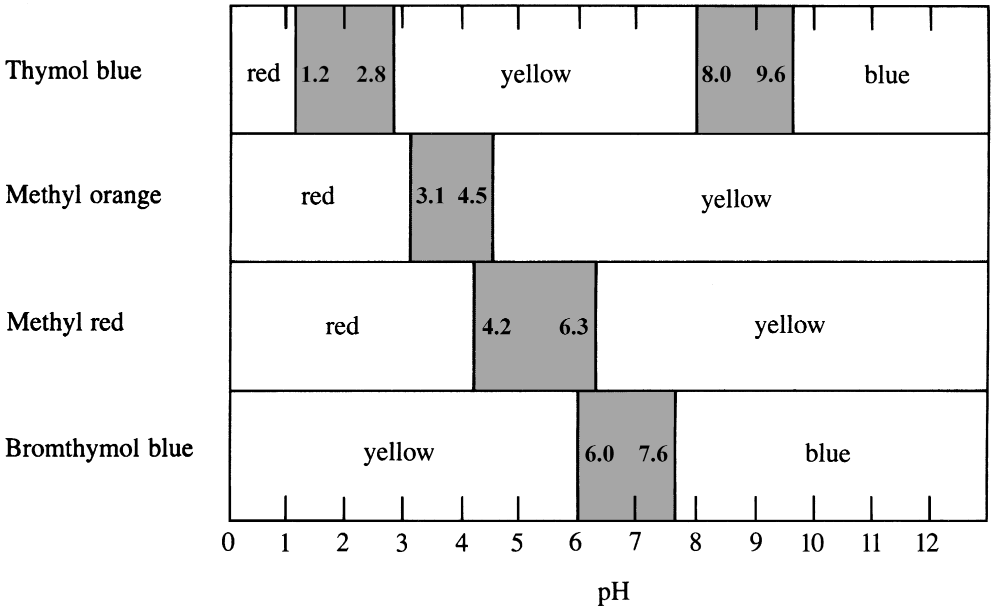
Consider the chart in Figure A.1, which gives the colors of four indicators as a function of pH. Returning to methyl orange, you will see from the chart that a solution containing this indicator will be red if the pH is less than 3.1, orange if the pH lies between 3.1 and 4.5, and yellow if the pH is 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.

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 so that each one will

FIGURE A.1
Color changes for four acid-base indicators. Shaded areas indicate the pH intervals in which the colors change.



change color at a different pH. The pH is estimated by moistening the paper with the solution being tested, 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 8 to 11 pH units (say, pH 1 to 11), whereas a short-range paper might cover only 2 or 3 pH units (say, pH 1 to 2.5).

pH Meter

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 H_3O^+ 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.