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Acid-Base Indicators and pH

Introduction

Acid-base indicators can be used to determine the pH of a solution. In this experiment, you will prepare your own acid-base indicator by extracting a colored plant pigment. Then you will use your indicator and others available in the lab to estimate the pH of several other solutions.

Acid-base indicators are substances that exist in different colored forms depending on pH. This behavior is possible because each acid-base indicator exists in conjugate acid and base forms. The following equilibrium between the acid form (“HIn”) and the base form (“In–”) of a hypothetical indicator exists in aqueous solutions:

$$\underset{\text{(blue)}}{HIn + H_2O} \rightleftharpoons \underset{\text{(red)}}{H_3O^+ + In^-}$$

Suppose that HIn is blue and In^- is red. We can use Le Châtelier’s principle to explain the color of this indicator in strongly acidic or basic solutions. If we add acid to the indicator solution, we will be adding excess H_3O^+. The reaction will proceed to the left to restore equilibrium, and red In^- will be converted to blue HIn. Therefore, this indicator will be blue in acidic solutions (with low pH). If we add base to the indicator solution, we will be removing H_3O^+. The reaction will proceed to the right to restore equilibrium, and blue HIn will be converted to red In^-. Therefore, this indicator will be red in basic solutions (with high pH). The exact pH range in which the indicator changes color depends on the equilibrium constant for the equilibrium between the acid and base forms of the indicator.

We can make our discussion more sophisticated by recognizing that indicators are *weak* acids and bases. Suppose that our hypothetical indicator has $K_{in} = 3 \times 10^{-5}$. Then, the following reactant-favored equilibrium between blue HIn and red In^- exists in acidic aqueous solutions:

$$\underset{\text{(blue)}}{HIn + H_2O} \rightleftharpoons \underset{\text{(red)}}{H_3O^+ + In^-} \qquad K_{in} = 3 \times 10^{-5}$$

Since the dissociation of HIn in water is reactant-favored, the indicator will be blue in acidic solutions. In basic aqueous solutions, the following equilibrium would exist:

$$OH^- + HIn \rightleftharpoons In^- + H_2O \qquad K = \frac{K_{in}}{K_w} = 3 \times 10^{+9}$$

Since the reaction of HIn with base is product-favored, the indicator will be red in basic solutions.

Suppose you put a tiny amount of this indicator into a solution that already has a certain pH. If the concentration of indicator is very small, the indicator itself will not noticeably change the pH of the solution. Rather, the relative amounts of the acid and base forms of the indicator will be determined by the pH and the value of K_{in}.

We can see this by rearranging the equilibrium constant expression for the indicator:

$$K_{in} = \frac{[H_3O^+][In^-]}{[HIn]} \qquad \text{so} \quad \frac{[\text{blue HIn}]}{[\text{red In}^-]} = \frac{[H_3O^+]}{K_{in}}$$

You can derive the same formula for the relative amounts of the acid and base forms in basic solutions, using the chemical equation for the equilibrium with OH^-, and remembering that $[H_3O^+]$ is equal to K_w divided by $[OH^-]$.

Table 9.1 below shows the relative amounts of the acid and base forms that will be present in solutions with increasing pH values. Unless the amounts of the acid and base forms differ by less than an order of magnitude, the color you will see is the color of the form with the higher concentration.

Displays of a number of different acid-base indicators will be available in the lab so that you can observe the colors over a wide range of pH values. The following discussion will help you to interpret the colors for a given indicator.

If you were to look at the display of our hypothetical indicator, you would see three different colors: blue, purple, and red. Without knowing about our theoretical predictions in Table 9.1, you might think that the indicator exists in three different chemical forms, each with different light-absorbing properties. But, if you look closely, you will see that the color that appears between the blue and the red forms is purple, a mixture of red and blue. At all pH's low and high, both the red and blue forms of the indicator are present. The pH determines the relative amount of each form present. At low pH (1 to 3), where the solution is very acidic, so little of the red form is present that it cannot be seen by the eye, and we say that the indicator is blue.

As the pH of the solution increases, the amount of the blue form in the solution decreases, and the amount of the red form increases. By pH 4, there is enough of the red form present to cause the solution to appear dark purple (mostly blue with some red). By pH 5, the amount of red form has increases relative to blue to the point where red predominates, and the solution appears light purple (mostly red with some blue). Above pH 5, there is so much red form compared to blue that only the red form can be seen. In other words, this particular indicator has only two chemical forms, each with its own color. The third observed color (purple) is a mixture of the other two colors.

Notice that when the indicator changes from one colored form to another, about 2 pH units are required to complete the change. The pH at the midpoint of the color change actually gives you an estimate of K_{in} for the indicator. At the pH at the midpoint of the color change, $[HIn] \approx [In^-]$, so $[H_3O^+] \approx K_{in}$. From your observations in this example, the midpoint of the color change must be somewhere between pH 4 and pH 5, so you would know that K_{in} is probably somewhere between 10^{-4} and 10^{-5}.

Table 9.1. Relative concentrations the acid and base forms of an indicator with K_{in} = 3×10^{-5} and predicted colors in solutions with increasing pH.

pH	$[H_3O^+]$ (M)	$\frac{[\text{blue HIn}]}{[\text{red In}^-]}$	Observed Color
1	10^{-1} (0.1)	$\frac{\text{3000 blue}}{\text{1 red}}$	blue
2	10^{-2} (0.01)	$\frac{\text{300 blue}}{\text{1 red}}$	blue
3	10^{-3} (0.001)	$\frac{\text{30 blue}}{\text{1 red}}$	probably still looks blue
4	10^{-4} (0.0001)	$\frac{\text{3 blue}}{\text{1 red}}$	probably looks dark purple (a mixture of blue and red)
5	10^{-5} (0.00001)	$\frac{\text{1 blue}}{\text{3 red}}$	probably looks light purple (a mixture of blue and red)
6	10^{-6} (0.000001)	$\frac{\text{1 blue}}{\text{30 red}}$	probably looks red
7	10^{-7} (0.0000001)	$\frac{\text{1 blue}}{\text{300 red}}$	red
8	10^{-8} (0.00000001)	$\frac{\text{1 blue}}{\text{3000 red}}$	red
9	10^{-9} (0.000000001)	$\frac{\text{1 blue}}{\text{30000 red}}$	red
10	10^{-10} (0.0000000001)	$\frac{\text{1 blue}}{\text{300000 red}}$	red

Some acid-base indicators have three different colored forms. These indicators are diprotic. *Practice Question:* What are the colors of the three forms of the following hypothetical indicator? Write two net ionic equations for the equilibria between H_2Ind, $HInd^-$, and Ind^{2-}: each equation should show the loss of just one proton. Estimate the equilibrium constant for each reaction.

pH	1	2	3	4	5	6	7	8	9	10	11	12	13
color	red	purple	purple	blue	blue	blue	blue	green	green	yellow	yellow	yellow	yellow

Answer: H_2Ind is red, $HInd^-$ is blue, and Ind^{2-} is yellow. Purple is a blend of the red and blue forms; green is a blend of the blue and yellow forms.

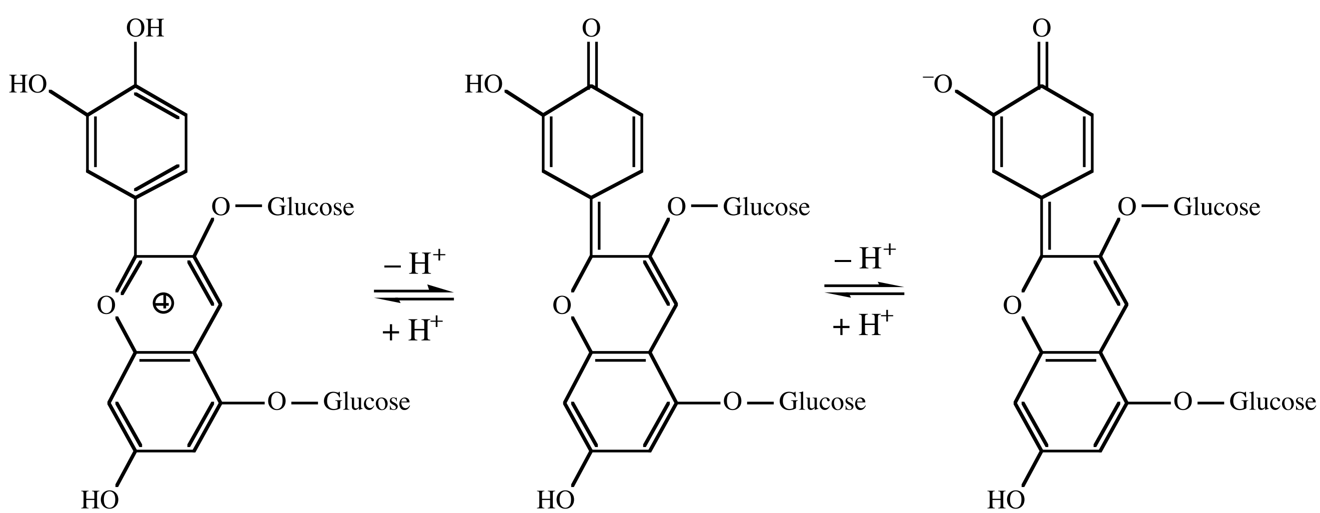
$H_2Ind + H_2O \rightleftharpoons H_3O^+ + HInd^-$ K is probably between 10^{-2} and 10^{-3}

$HInd^- + H_2O \rightleftharpoons H_3O^+ + Ind^{2-}$ K is probably between 10^{-8} and 10^{-9}

Indicators from Plant Extracts

The many shades of blue, purple, violet, and most of the red that appear in flowers, fruits, leaves, and stems of plants are due to one or more of the group of pigments called *anthocyanins* dissolved in the cell sap. There are a number of different anthocyanins, such as cyanin shown in Figure 9.1, but they are all very similar chemically.

Figure 9.1. The three forms of cyanin, a plant pigment that behaves as an acid-base indicator.



cyanin cation (pH < 3, red) cyanin base (pH 6–8, violet) cyanin anion (pH > 11, blue)

As shown in the equations in Figure 9.1, the anthocyanins will undergo acid-base reactions with accompanying changes in color, thus fulfilling at least some of the requirements for an acid-base indicator. This property has been used to advantage by wine makers, who have titrated wine for its total acidity, using the color change from red to green as an endpoint. It has been suggested that color changes occurring during the ripening of fruits may be related to colors in pH. It is materials of this sort, either plant extracts or synthetic dyes, which are used in the pH-indicating papers and pH-indicating solutions that you will be using in the laboratory.

Experimental Procedure

SAFETY PRECAUTIONS: Wear your SAFETY GOGGLES. If you decide to make an indicator from flower petals and ethanol, heat the mixture on a hot plate in the fume hood, not over a Bunsen burner.

WASTE DISPOSAL: Put all solid waste, such as boiled cabbage leaves in the trash cans. All liquid waste from this experiment should be poured down the drain, followed by plenty of running water.

Part I. Observing displays of commercial indicators

Carefully examine the indicators displayed in the laboratory. Record the name of each indicator, and the color at each pH value. How many different chemical forms does each one have? What are the different colors of the different forms? Remember that some of the colors you see are only blends (mixtures). Estimate the equilibrium constants for the dissociation of the acid form(s) of each indicator.

Part II. Making your own acid-base indicator

You may use the provided red cabbage leaves for your indicator, or you may bring in your own naturally colored materials to use instead.

Some fruit and vegetable pigments that exhibit indicator behavior are: red apple, blackberry, blueberry, red cabbage, cactus, cherry, cranberry, grape, loganberry, red onion, plum, pomegranate, raspberry, rhubarb, strawberry, and black tea. You may also experiment with other fruits and vegetables that are not on this list. (Some fruit and vegetable pigments that *do not* exhibit indicator behavior are: apricot, carrot, peach, pear, persimmon, and tomato.)

Some flower pigments that exhibit indicator behavior are: begonia, clover (red), geranium, lily, pansy, rose (red, pink, white, and yellow), violet. You also may experiment with flowers that are not on this list.

To extract the pigments of a fruit or vegetable, use the colored part and discard the rest (*i.e.*, use the skins only, in the case of grapes or apples). Break the colored material into very small pieces, and put them into a *clean* small beaker. Add enough purified water to just cover the material. Heat the mixture for 10-15 minutes. Allow it to cool, and pour off the liquid into a clean test tube or beaker. Filter the liquid if it is cloudy. (Note: Red cabbage does not need to be heated as much as some of the other materials. A mixture of water and red cabbage leaves should be heated until it begins to boil, and then allowed to steep for a few minutes until the liquid becomes dark purple.)

If you would like to use berries, crush the raw fruit and press out the juice. Then add an equal volume of 95% ethanol as a preservative, and filter.

If you would like to use flower petals, heat the petals in a small amount of ethanol (use a hot plate) to give a colored extract.

In every case, these natural indicators are inferior to commercial products because they undergo an irreversible decomposition, giving a brown color, when kept for some time in basic solution.

To see what color your indicator has at each pH, set up a display rack like those in the lab, with each test tube labeled for a given pH. Pour enough pH solution into each test tube to give a depth of about one-half inch (estimate this; don't bother to measure), and then add about 4 drops of your indicator to each test tube. Record the color of the your plant pigment indicator at each pH. If your colored material happens not to exhibit indicator behavior, also describe another student's display.

How many different chemical forms of the plant pigment do you think are responsible for all the colors you see? (Allow for blends where the colors overlap.) Estimate the equilibrium constants for the dissociation of the acid form(s) of your indicator. What is the pH of the plant when you buy it in the store? Compare the original color of the plant pigment with the colors in your test tube display.

Part III. Using the indicators to determine pH of common solutions

In this part of the experiment, you are to find the pH of at least <u>four</u> different solutions. Two of them must be colorless unknown solutions from the numbered bottles in the hood, and two must be common "household" solutions. These household solutions could be saliva, tap water, distilled water, hand soap, vinegar, household ammonia, stomach acid (use 0.01 M HCl), hard water (use saturated calcium sulfate solution), very weak tea, or any other solution that does not have a pronounced color of its own. Some of these will be provided in the lab. You may also bring in your own solutions to test. These must be drain-disposable aqueous solutions.

To find the pH of an unknown solution:

Choose one of the acid-base indicators whose color at various pH values are on display. (You might choose the indicator that you made yourself.) Record the name of the indicator that you choose. Pour a small amount (up to 1/2 inch depth) of the solution of unknown pH into a clean, rinsed test tube. Record the color of the unknown solution.

To it, add about 4 drops of the indicator you have arbitrarily chosen. Record the new color of the solution. Draw a conclusion from your observations. What have you learned about the range of possible pH values for the unknown? Decide on a second indicator.

In another test tube, take a fresh sample of your unknown. Add about 4 drops of the second indicator. Record the name of the second indicator and the color of the indicator in your unknown solution. Draw a conclusion from your observations. What have you learned about the range of possible pH values for the unknown? Decide on a third indicator.

Continue to test fresh portions of the unknown solution (in clean test tubes) with different indicators until you have narrowed the pH range down as much as possible with the indicators provided. As you work, record which indicators you use, the colors you observe, and the conclusions you draw from your observations.