Learning Objectives

- Explain color changes of indicators.
- Determine the acidic dissociation constants $K_a$ or $K_{ai}$ of indicators.

**Indicators** are substances whose solutions change color due to changes in pH. These are called acid-base indicators. They are usually weak acids or bases, but their conjugate base or acid forms have different colors due to differences in their absorption spectra. Did you know that the color of hydrangea flowers depends on the pH of the soil in which they are grown?

![Image of hydrangea flowers](https://via.placeholder.com/150)

Figure \(\PageIndex{1}\): This picture shows various colors of hydrangea flowers. (CC BY-SA 4.0 International; FlowerPowerH2020 via Wikipedia).

Indicators are organic weak acids or bases with complicated structures. For simplicity, we represent a general indicator by the formula \(\text{\textcolor{Blue}{HIn}}\), and its ionization in a solution by the equilibrium,

\[
\text{\textcolor{Blue}{HIn}} \rightleftharpoons \textcolor{Red}{H^+} + \text{\textcolor{Red}{In^-}}
\]

and define the equilibrium constant as $K_{ai}$,

\[
[K_{\text{\textcolor{Red}{In^-}}}] = \dfrac{[\textcolor{Red}{In^-}]}{[\text{\textcolor{Blue}{HIn}}]} = \dfrac{K_{ai}}{[\text{\textcolor{Red}{H^+}}]}
\]

which can be rearranged to give

\[
\dfrac{[\text{\textcolor{Red}{In^-}}]}{[\text{\textcolor{Blue}{HIn}}]} = \dfrac{K_{ai}}{[\text{\textcolor{Red}{H^+}}]}
\]

When \(\text{ice}([\text{\textcolor{Red}{H^+}}])\) is greater than 10 $K_{ai}$, \(\text{\textcolor{Red}{In^-}}\) color dominates, whereas color due to \(\text{\textcolor{Blue}{HIn}}\) dominates if \(\text{ice}([\text{\textcolor{Red}{H^+}}]) < \dfrac{K_{ai}}{10}\). The above equation indicates that the color change is the most sensitive when \(\text{ice}([\text{\textcolor{Red}{H^+}}]) = K_{ai}\) in numerical value.

We define $pK_{ai} = - \log(K_{ai})$, and the $pK_{ai}$ value is also the pH value at which the color of the indicator is most sensitive to pH changes.
Taking the negative log of $K_{\text{ai}}$ gives,

\[-\log K_{\text{ai}} = -\log c_{\text{[H+]}} - \log \frac{[\text{In}^-]}{[\text{HIn}]}\]

or

\[\text{pH} = pK_{\text{ai}} + \log \frac{[\text{In}^-]}{[\text{HIn}]}\]

This is a very important formula, and its derivation is very simple. Start from the definition of the equilibrium constant $K$; you can easily derive it. Note that $\text{pH} = pK_{\text{ai}}$ when $[\text{In}^-] = [\text{HIn}]$. In other words, when the pH is the same as $pK_{\text{ai}}$, there are equal amounts of acid and base forms. When the two forms have equal concentration, the color change is most noticeable.

Colors of substances make the world a wonderful place. Because of the colors and structures, flowers, plants, animals, and minerals show their unique characters. Many indicators are extracted from plants. For example, red cabbage juice and tea pigments show different colors when the pH is different. The color of tea darkens in a basic solution, but the color becomes lighter when lemon juice is added. Red cabbage juice turns blue in a basic solution, but it shows a distinct red color in an acidic solution.

Common Indicators: Some common indicators and their $pK_{\text{ai}}$ values are given in a table form.

<table>
<thead>
<tr>
<th>Name</th>
<th>Acid Color</th>
<th>pH Range of Color Change</th>
<th>Base Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl violet</td>
<td>Yellow</td>
<td>0.0 - 1.6</td>
<td>Blue</td>
</tr>
<tr>
<td>Thymol blue</td>
<td>Red</td>
<td>1.2 - 2.8</td>
<td>Yellow</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>Red</td>
<td>3.2 - 4.4</td>
<td>Yellow</td>
</tr>
<tr>
<td>Bromocresol green</td>
<td>Yellow</td>
<td>3.8 - 5.4</td>
<td>Blue</td>
</tr>
<tr>
<td>Methyl red</td>
<td>Red</td>
<td>4.8 - 6.0</td>
<td>Yellow</td>
</tr>
<tr>
<td>Litmus</td>
<td>Red</td>
<td>5.0 - 8.0</td>
<td>Blue</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>Yellow</td>
<td>6.0 - 7.6</td>
<td>Blue</td>
</tr>
<tr>
<td>Thymol blue</td>
<td>Yellow</td>
<td>8.0 - 9.6</td>
<td>Blue</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>Colorless</td>
<td>8.2 - 10.0</td>
<td>Pink</td>
</tr>
<tr>
<td>Thymolphthalein</td>
<td>Colorless</td>
<td>9.4 - 10.6</td>
<td>Blue</td>
</tr>
<tr>
<td>Alizarin yellow R</td>
<td>Yellow</td>
<td>10.1 - 12.0</td>
<td>Red</td>
</tr>
</tbody>
</table>

There is a separate file for this, and it can also be accessed from the Chemical Handbook menu.

Example $\PageIndex{1}$
Find an indicator for the titration of a 0.100 M solution of a weak acid $\ce{HA}$ ($K_a = 6.2 \times 10^{-6}$) with 0.100 M $\ce{NaOH}$ solution.

**SOLUTION**

First, you should estimate the pH at the equivalence point, at which the solution is 0.0500 M $\ce{NaA}$. This is a hydrolysis problem, but the following method employs the general principle of equilibrium.

\[
\begin{array}{ccccccc}
\ce{A- + H2O &\rightleftharpoons HA + OH-} \\
0.0500-y & & & y & & y
\end{array}
\]

If we multiply the numerator and the denominator by $\ce{[H+]\times[OH-]}$, rearrange the terms, note that $\ce{[H+]\times[OH-]} = K_w$, and by the definition of $K_a$ of the acid, we have the following relationship:

\[
\frac{y^2}{0.0500-y} = K_w \times \frac{K_a}{K_w}
\]

\[
\begin{align*}
y &= \left(0.0500 \left(\frac{K_w}{K_a}\right)\right)^{1/2} \\
&= 9.0 \times 10^{-6}
\end{align*}
\]

\[
\begin{align*}
\ce{pOH} &= -\log \ce{[OH-]} = -\log 9.0 \times 10^{-6} \\
&= 5.05
\end{align*}
\]

\[
\begin{align*}
\ce{pH} &= 14 - 5.05 \\
&= 8.95
\end{align*}
\]

Phenolphthalein in the table above has a $pK_{ai}$ value of 9.7, which is the closest to the pH of equivalence point in this titration. This indicator is colorless in acidic solution, but a light PINK appears when the pH is > 8. The color becomes more INTENSE PINK as the pH rises. A parade of the color intensities is shown below:

The equivalence point is when the color changes most rapidly, not when the solution has changed color. Improper use of indicators will introduce inaccuracy to titration results.

**Colors of an Indicator Solution**

Indicators change color gradually at various pH. Let us assume that the acid form has a blue color and the basic form has red color. The variation of colors at different pH is shown below. The background color affects their appearance and our perception of them.
The long stretched color in the middle of the last line has equal intensity of **BLUE** and **RED**. If a solution has a color matching this, the pH would be the same as the \( pK_{ai} \) of the indicator, provided that the conjugate forms of the indicator have the **BLUE** and **RED** colors.

**Questions**

1. There are numerous natural indicators present in plants. The dye in red cabbage, the purple color of grapes, even the color of some flowers are some examples. What is the cause for some fruits to change color when they ripen?

2. Choose the true statement:
   a. All weak acids are indicators.
   b. All weak bases are indicators.
   c. Weak acids and bases are indicators.
   d. All indicators are weak acids.
   e. An acid-base conjugate pair has different colors.
   f. Any indicator changes color when the pH of its solution is 7.

3. Do all indicators change color at pH 7 (y/n)?

**Solutions**

1. *Answer* \( \ce{[H+]}}) of the juice changes.
   *Hint...*
   The changes in pH or \( \ce{[H+]}}) cause the dye to change color if their conjugate acid-base pairs have different colors. There may be other reasons too. Do colors indicate how good or bad they taste?

2. *Answer* d.
   *Hint...*
   Color change is a requirement for indicators.

3. *Answer* No!
   *Hint...*
   Phenolphthalein changes color at pH \(~9\). Bromothymol blue has a \( pK_r \) value of 7.1. At pH 7, its color changes from yellow to blue. Some indicators change color at pH other than 7.
Contributors

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