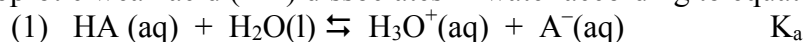


Chem 151L. Indicators and Simple Acid-Base Calculations

The Acid Dissociation Constant, K_a

A monoprotic weak acid (HA) dissociates in water according to equation (1):



The acid dissociation expression is:

$$(2) K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

From this expression we can derive the simple Henderson-Hasselbach equation for a weak acid:

$$(3) \text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right)$$

The reaction between a base (such as NaOH) and a weak acid is given below:



The equilibrium constant for this reaction, K_T , is much larger than one ($K_T \gg 1$). What is the relationship between K_T and K_a ? At the "half-way to equivalence point" exactly one half of a monoprotic weak acid has reacted with hydroxide. At this point, the amount of HA remaining is exactly equal to the amount of conjugate ion, A^- , formed. The ratio $[\text{A}^-] / [\text{HA}]$ in equation (4) is equal to one and $\log(1)$ is equal to zero. So equation (4) becomes:

$$(5) \text{pH} = \text{p}K_a \text{ (at the half-way to equivalence point)}$$

At the equivalence point, the moles of weak acid are equal to the moles of OH^- added. The pH of the solution at the equivalence point is the same as that of a solution created from the weak acid salt (See the Handouts for more details on the equivalence point pH calculation).

Indicators

Indicators are weak organic acids (HIn) that change color when deprotonated (In^-). A few drops of indicator added to the analyte solution before the beginning an acid-base titration. When enough base titrant is added to the analyte solution the equilibrium expressed in equation 1 will shift toward products.



The result is the formation of more of the deprotonated indicator (In^-) and a corresponding color change of the analyte solution (the endpoint). A good indicator for a specific acid-base titration has $\text{p}K_a$ at or near the pH of the equivalence point.

The equation 3 in the ***Acid-Base Calculations*** part can be rewritten as:

$$(2) \text{p}K_a = \text{pH} - \log \left(\frac{[\text{In}^-]}{[\text{HIn}]} \right)$$

An examination of Equation 2 suggests that if we are able to monitor the relative concentrations of HIn and In^- , it should be possible to determine the K_a for the indicator. The approach used in this experiment involves taking advantage of the fact that the acidic (HIn) and basic (In^-) forms of the indicator absorb more strongly at different wavelengths.

By monitoring the change in absorbance of each form as a function of solution pH, it is possible to extract a value for the K_a of the indicator. From equation 2, the solution pH will be equal to the $\text{p}K_a$ of the indicator when the concentrations of HIn and In^- in solution are equivalent. Experimentally, this corresponds to the pH where the absorbance of each form is half of its maximum absorbance. At this point, half of the initial number of moles of HIn have been converted to an equivalent number of moles of In^- . As a result, the concentrations of each species are equal and the log term in Equation 2 becomes zero. Consequently, the $\text{p}K_a$ of an indicator corresponds to the pH of the solution at the inflection point in a plot of absorbance as a function

of pH as shown in Figure 1. Note, however, that it is critical that the absorbance at each wavelength corresponds to the absorbance of only HIn at λ_1 and only In^- at λ_2 .

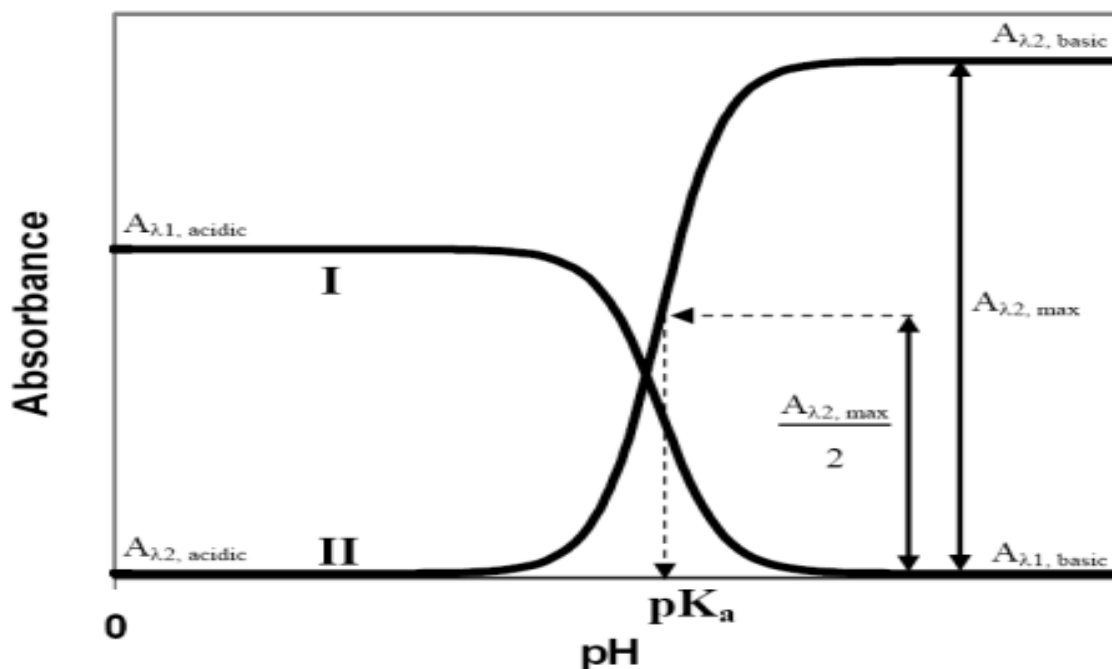
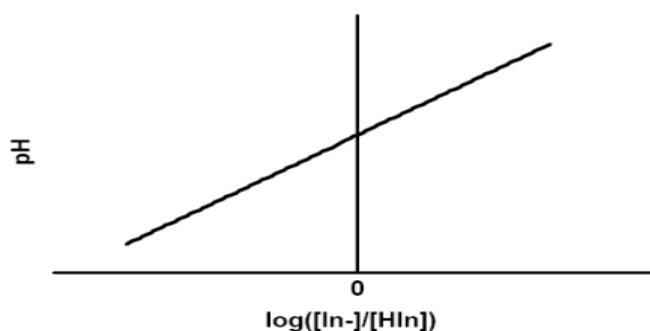


Fig. 1, A plot of absorbance as a function of pH for an indicator. I- measurements which are made at a wavelength (λ_1) at which HIn absorbs radiation; II - measurements which are made at a wavelength (λ_2) at which In^- absorbs radiation.

Rearranging equation 2 results in the most common form of the Henderson-Hasselbach equation for the indicator. This expression provides an alternative way to determine the pK_a of an indicator by plotting pH (y axis) as a function of $\log([\text{In}^-]/[\text{HIn}])$. As shown in Figure 2, the resulting straight line intersects the pH axis when pH equals pK_a .

Fig. 2, A plot of pH as a function of $\log([\text{In}^-]/[\text{HIn}])$. The pK_a of the indicator corresponds to the intersection of the line with the pH axis

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right)$$



It is possible to obtain the ratio $[\text{In}^-]/[\text{HIn}]$ to use for the plot from spectrophotometric measurements which are made at two wavelengths. The first wavelength (λ_1) is chosen where the acidic (HIn) but not the basic form (In^-) of the indicator strongly absorbs radiation. The second wavelength (λ_2) is chosen where the basic but not the acid form strongly absorbs radiation. If Beer's law is obeyed, the absorbance at λ_1 and λ_2 are:

$$(3) \quad A_{\lambda_1} = \epsilon_{(\text{HIn}, \lambda_1)} \cdot b \cdot [\text{HIn}]$$

$$(4) \quad A_{\lambda_2} = \epsilon_{(\text{In}^-, \lambda_2)} \cdot b \cdot [\text{In}^-]$$

where A is absorbance, ϵ is molar absorptivity and b is cell pathlength. At any pH, the total concentration (C_T) of both forms of the indicator is constant and the sum of the individual concentrations of each species.

$$(5) \quad C_T = [\text{HIn}] + [\text{In}^-]$$

In solutions of low pH, essentially all of the indicator is in the acid form. Consequently, in highly acid solutions, $C_T = [\text{HIn}]$, and

$$(6) \quad A_{\lambda_1, \text{acidic}} = \epsilon_{(\text{HIn}, \lambda_1)} \cdot b \cdot C_T$$

In highly basic solutions essentially all of the indicator is in the basic form and $C_T = [\text{In}^-]$ so that

$$(7) \quad A_{\lambda_2, \text{basic}} = \epsilon_{(\text{In}^-, \lambda_2)} \cdot b \cdot C_T$$

Taking a ratio of equations (3) to (6) and (4) to (7) provides expressions for the fraction of the indicator present in each form:

$$(8) \quad A_{\lambda_1} / A_{\lambda_1, \text{acidic}} = [\text{HIn}] / C_T$$

$$(9) \quad A_{\lambda_2} / A_{\lambda_2, \text{basic}} = [\text{In}^-] / C_T$$

The ratio $[\text{In}^-]/[\text{HIn}]$ at any pH can be obtained by dividing equation (8) by equation (9) to give:

$$(10) \quad [\text{In}^-]/[\text{HIn}] = (A_{\lambda_2} \cdot A_{\lambda_1, \text{acidic}}) / (A_{\lambda_1} \cdot A_{\lambda_2, \text{basic}})$$

Bromthymol blue acts as a weak acid in solution. It can thus be in protonated or deprotonated form, appearing yellow or blue respectively. It is bluish green in neutral solution. The deprotonation of the neutral form results in a highly conjugated structure, accounting for the difference in color. The absorbance of a bromthymol blue solution is measured as the solution's pH is varied. As the solution pH changes from acidic to basic, we observe an evolution from spectra (Fig. 3) where the peak centered around 430 nm (denoted by λ_1) is largest, to spectra where the peak at about 630 nm (denoted by λ_2) dominates.

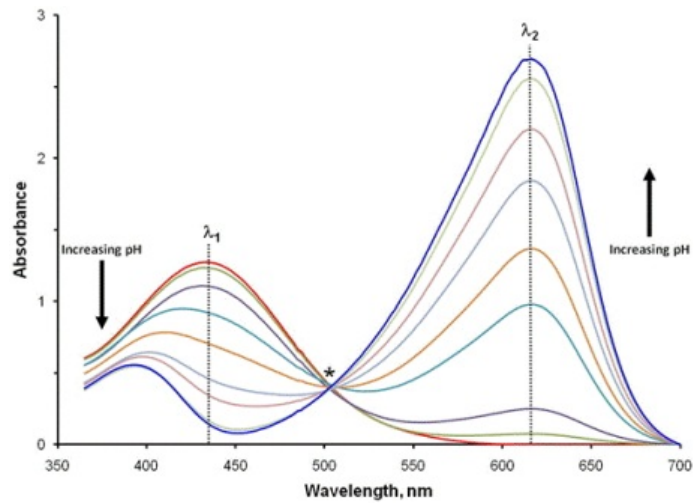


Fig. 3, Spectra of the indicator bromothymol blue as a function of pH.

Buffer Solutions

Buffer Solutions are mixtures of weak organic acids (HA) and weak acid salts (NaA) that fix the pH of a solution via the Henderson-Hasselbach equation.