Contents

Chapter 15

Acids & Bases

15.1 Acids

Historically, an acid has been a compound that dissociates in aqueous media (water that is) to yield hydrogen ions, H^+ (protons).

$$AH^+ \longrightarrow A^- + H^+$$

Acids have a characteristic sour taste and in concentrated form strong acids "eat" clothes and skin. Indeed, the reaction between nitric acid and protein to form a brown colored product is a test for protein.

15.1.1 Measurement of Acid: pH

The classical neutralization of the classical acid, the proton: H^+, by the classical base, hydroxide: OH^-, is

$$H^+ + OH^- \Rightarrow H_2O$$

Or this may be written as the dissociation of water

$$2H_2O \Longrightarrow H_3O^+ + OH^-$$

An equilibrium constant for this reaction is

$$K_w = [H_3O^+][OH^-] = 10^{-14}M^2$$

Since the range of chemically useful hydrogen ion concentrations covers many decades in concentration it has become convenient to use a log scale. So pH is defined by

$$pH = -\,log\,[H^+]$$

Since equilibrium constants also vary over many orders of magnetude it is convenient to define a pK for acids and bases.

$$pK = -\,log\,K$$

If we take the log of the equilibrium constant expression for the dissociation of water we get

$$log\,K_w = -14 = log\,[H_3O^+] + log\,[OH^-]$$
$$or$$
$$pK_w = 14 = pH + pOH$$

Where we have defined pOH as

$$pOH = -\,log\,[OH^-]$$

example

The hydrogen ion concentration is 0.1M in aqueous solution. What is the pH and the pOH? pH = -log 0.1 = 1 and pOH = 14 - pH = 13.

15.2 Strength of Acids and Bases

The designation of acids and bases as strong or weak is qualitative. We need to make these designations more precise. These acid-base chemical reactions, at equilibrium, may be represented by equilibrium constant expressions. For example,

$$H_2CO_3 + H_2O \longrightarrow H_3O^+ + H_CO_3^-$$
$$K_{a_1} = \frac{[H_3O^+][H_CO_3^-]}{[H_2CO_3]} = 4.2 \times 10^{-7}$$
$$H_CO_3^- + H_2O \longrightarrow H_3O^+ + CO_3^{2-}$$
$$K_{a_2} = \frac{[H_3O^+][CO_3^{2-}]}{[H_3O^+][HCO_3^-]} = 5.6 \times 10^{-11}$$

The magnitude of the equilibrium constant is a measure of the abiliity of the acid or base to dissociate (in aqueous media). The smaller the constant the weaker the acid or base.

For the first dissociation of carbonic acid $pK_{a_1} = 6.38$ and for the second $pK_{a_2} = 10.25$. In this example of the dissociation of carbonic acid the equilibrium constant for the first dissociation of a proton is much greater than the equilibrium constant for the dissociation of the second proton. This makes physical sense because it is obviously harder to remove a second protron leaving behind two negative charges on a single molecule, CO_3^{--}.

15.2.1 Strong Acids

The following examples are members of acids that are strongly dissociated in water or simply *strong acids.*

$$hydrochloric\ acid : HCl + H_2O \Rightarrow H_3O^+ + Cl^-$$
$$nitric\ acid : HNO_3 + H_2O \Rightarrow H_3O^+ + NO_3^-$$
$$sulfuric\ acid : H_2SO_4 + H_2O \Rightarrow H_3O^+ + HSO_4^-$$
$$H_SO_4^- + H_2O \Rightarrow H_3O^+ + SO_4^{2-}$$

15.3 Dissociation of a Strong Acid

15.3.1 Sulfuric Acid

Quick and Dirty Method

If we assume that sulfuric acid *completely* dissociates in water we are lead to

$$H_2SO_4 + 2H_2O \longrightarrow 2H_3O^+ + SO_4^{2-}$$

and if the orignial concentration of sulfuric acid in water were 0.1 molar then we would expect $[H_3O^+] = 0.2$ molar since for each mole of the acid two moles of protons result.

This estimation has tacitly assumed that the equilibrium constants for the dissociation of the acid are infinite. If this assumption is good enough then our calculation is sufficently accurate. In any case we have an order of magnetude of the acid concentration.

More Exact Method

The dissociation of sulfuric acid in water yields the following species and ions H_3O^+, OH^-, H_2SO_4, HSO_4^- , SO_4^{2-} and the determination of the concentrations of these five species requires five independent equations.

The equilibrium constant expressions may be written as

$$\begin{aligned} H_2SO_4 + H_2O &\Leftrightarrow HSO_4^- + H_3O^+ \\ K_{a_1} &= \frac{[HSO_4^-][H_3O^+]}{[H_2SO_4]} = \infty \\ HSO_4^- + H_2O &\Leftrightarrow SO_4^{2-} + H_3O^+ \\ K_{a_2} &= \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]} = 0.012 \\ the\ dissociation\ of\ water & \\ K_w &= [H^+][OH^-] = 1.0 \times 10^{-14} \end{aligned}$$

More Refined Quick and Dirty Method

Since the second equilibrium constant is not really huge we can focus on this equilibrium. Consider that the first dissociation gives a contribution to $[H_3O^+]$ of 0.1M and the concentration of $[HSO_4^-] = 0.1$M. If x moles per liter of this dissociates then

$$\begin{array}{ccc} [HSO_4^-] \longrightarrow & H_3O^+ + & SO_4^{2-} \\ 0.1 - x & 0.1 + x & x \end{array}$$

and

$$\frac{x(0.1+x)}{0.1-x} = K_{a_2} \qquad or\ x \approx K_{a_2}$$

where we are assuming we can neglect x with respect to 0.1. We have to check this approximation later. From this x = 0.012M which is a bit smaller than 0.1 so let us live with this. Now $[H^+] = 0.1$ (from the first dissociation) + 0.012 = 0.112M.

Now back to the "More Exact Method."

If the initial concentration of sulfuric acid in moles per liter is $C_{H_2SO_4}$ then mass balance is given by

$$C_{H_2SO_4} = [H_2SO_4] + [HSO_4^-] + [SO_4^{2-}]$$

Electrical neutrality, or charge balance, gives

$$[H^+] = [OH^-] + [HSO_4^-] + 2[SO_4^{2-}]$$

where the factor 2 indicates that for each mole of SO_4^{2-} there are two electrical charges.

Using the equilibrium constant expressions for $[H_2SO_4]$ and $[HSO_4^-]$ and substituting into the mass balance equation gives

$$C_{H_2SO_4} = \frac{[HSO_4^-][H_3O^+]}{K_{a_1}} + [HSO_4^-] + [SO_4^{2-}]$$

$$C_{H_2SO_4} = [SO_4^{2-}]\left\{\frac{[H_3O^+]}{K_{a_1}}\frac{[H_3O^+]}{K_{a_2}} + \frac{[H_3O^+]}{K_{a_2}} + 1\right\}$$

and from charge balance

$$[H_3O^+] = \frac{K_w}{[H_3O^+]} + [SO_4^{2-}]\left\{\frac{[H_3O^+]}{K_{a_2}} + 2\right\}$$

We may solve for $[SO_4^{2-}]$ using the charge balance expression and substitute into the mass balance equation to obtain

$$\left\{[H_3O^+] - \frac{K_w}{[H_3O^+]}\right\}\left\{\frac{[H_3O^+]}{K_{a_1}}\frac{[H_3O^+]}{K_{a_2}} + \frac{[H_3O^+]}{K_{a_2}} + 1\right\} = \left\{\frac{[H_3O^+]}{K_{a_2}} + 2\right\} \times C_{H_2SO_4}$$

This algebraic equation may be solved as a cubic equation in $[H^+]$.

Let us apply approximations. First, we have an acidic solution and we expect that $[H_3O^+] >> \frac{K_w}{[H_3O^+]}$ so we may neglect $\frac{K_w}{[H_3O^+]}$. Secondly $K_{a_1} = \infty$ and $\frac{1}{K_{a_1}} = 0$ and the equation reduces to:

$$\left\{[H_3O^+]\right\}\left\{\frac{[H_3O^+]}{K_{a_2}} + 1\right\} = \left\{\frac{[H_3O^+]}{K_{a_2}} + 2\right\} \times C_{H_2SO_4}$$

If we assumed that both ionizations were complete, that the acid was very "strong", then $K_{a_2} = \textit{very large}$ and $\frac{1}{K_{a_2}} \to 0$ and we could neglect these terms giving

$$\left\{[H_3O^+]\right\}\{1\} = \{2\} \times C_{H_2SO_4}$$

or $[H_3O^+] = 2 \times C_{H_2SO_4}$ the value for our original assumption of a completly dissociated sulfuric acid.

However, we have $k_{a_2} = 0.012$ and if $[H_3O^+] \approx 0.1 - 0.2$ then $\frac{[H_3O^+]}{K_{a_2}} \approx 8 - 16$ and cannot be neglected with respect to 1 or 2. We must keep these terms.

$$\frac{[H_3O^+]^2}{K_{a_2}} + [H_3O^+] - \left\{\frac{[H_3O^+]}{K_{a_2}} + 2\right\} \times C_{H_2SO_4} = 0$$

This quadratic equation in $[H_3O^+]$ gives

$$\frac{2}{K_{a_2}}[H_3O^+] = -(1 - \frac{C_{H_2SO_4}}{K_{a_2}}) \pm \sqrt{(1 - \frac{C_{H_2SO_4}}{K_{a_2}})^2 + 8\frac{C_{H_2SO_4}}{K_{a_2}}}$$

If $C_{H_2SO_4} = 0.1$ then we get $[H^+] = 0.11$M for the hydrogen ion concentration from the dissociation of H_2SO_4. This is the right order of magnetude, but quite a different result from the assumption of complete dissociation made at the start. We obtain about 10% error due to the simple consideration of the dissociation of HSO_4^- in the second approximation.

What should be done? First, the quick and dirty method gives the order of magnetude for the hydrogen ion concentration. Second, note the size of the equilibrium constants. Here we will be lead to consider the second dissociation HSO_4^- and do a quick and dirty calculation using that. In this example the starting concentration for HSO_4^- is from the first dissociation as is a contribution to H_3O^+ and we use $[HSO_4^-] = 0.1 - x$; $[H_3O^+] = 0.1 + x$ and $[SO_4^-] = x$ substitute this into the equilibrium constant expression, neglect x with respect to 0.1 - check this later - and solve for x. The result is within 10% and that is good enough!

15.3.2 Weak Acids

Another obvious extreme are acids that are weakly dissociated in water or *weak acids* and examples of weak acids are

$$\begin{aligned}
acetic\ acid: CH_3COOH + H_2O &\Rightarrow H_3O^+ + CH_3COO^- \quad K_a = 1.74 \times 10^{-5} \\
hydrocyanic\ acid: HCN + H_2O &\Rightarrow H_3O^+ + CN^- \quad K_a = 4.0 \times 10^{-10} \\
carbonic\ acid: H_2CO_3 + H_2O &\Rightarrow H_3O^+ + H_CO_3^- \quad K_{a_1} = 4.2 \times 10^{-7} \\
H_CO_3^- + H_2O &\Rightarrow H_3O^+ + CO_3^{2-} \quad K_{a_2} = 5.6 \times 10^{-11} \\
phosphoric\ acid: H_3PO_4 + H_2O &\Rightarrow H_3O^+ + H_2PO_4^- \quad K_{a_1} = 5.9 \times 10^{-3} \\
H_2PO_4^- + H_2O &\Rightarrow H_3O^+ + HPO_4^{2-} \quad K_{a_2} = 6.2 \times 10^{-8} \\
HPO_4^{2-} + H_2O &\Rightarrow H_3O^+ + PO_4^{3-} \quad K_{a_3} = 4.8 \times 10^{-13}
\end{aligned}$$

15.3.3 Dissociation of Acetic Acid

The dissociation of acetic acid in water is

$$HOAc + H_2O \longrightarrow H_3O^+ + OAc^- \quad K_a = \frac{[OAc^-][H^+]}{[HOAc]} = 1.74 \times 10^{-5}$$

Quick and Dirty Method

We assume that acetic acid *weakly* dissociates in water because it's equilibrium constant is small. If the orignial concentration of the acid in water is 0.1 molar then we expect some small amount, x, to dissociate and

$$\begin{aligned}
[HOAc] &= 0.1 - x \\
&and \\
[H_3O^+] &= x \\
[OAc^-] &= x
\end{aligned}$$

$$HOAc + H_2O \longrightarrow H_3O^+ + OAc^- \qquad K_a = \frac{[OAc^-][H^+]}{[HOAc]} = 1.74 \times 10^{-5}$$

$$0.1 - x \qquad\qquad x \qquad x$$

$$K_a = \frac{x^2}{0.1 - x}$$

and if we can neglect x with respect to 0.1 we have $x = \sqrt{0.1K_a} = 1.32 \times 10^{-3}$ and pH = 2.88. Since $1.32 \times 10^{-3} << 0.1$ the approximation is justified. [1]

15.4 Bases

A base is a compound that neutralizes an acid and classically that has been by OH^-, hydroxyl ion. The neutralization reaction is

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

Bases may also be classified as strong or weak depending on the degree of dissociation.

15.4.1 Strong Bases

$$sodium\ hydroxide : NaOH + H_2O \Rightarrow Na^+ + OH^-$$

15.4.2 Weak Bases

$$ammonia : NH_3 + H_2O \Rightarrow NH_4^+ + OH^- \qquad K_b = 1.74 \times 10^{-5}$$
$$hydroxylamine : HONH_2 + H_2O \Rightarrow HONH_3^+ + OH^- \qquad K_b = 9.1 \times 10^{-9}$$

15.5 Generalized Acids and Bases

The classic view of an acid base reaction if the neutralization of H_3O^+ by OH^- to form water.

$$H_3O^+ + OH^- \longrightarrow H_2O$$

We might look at this in a more general way. The proton, H^+, likes to accept an electron. Let us define a "Lewis Acids" acid as a compound that accepts an unshared pair of electrons. Using this chemical idea we may classify acids and their conjugate bases as the following example show.

[1]We will consider exact calculations elsewhere.

$$\underset{acid}{H_3O^+} + \underset{base}{NH_3} \rightarrow \underset{acid}{NH_4^+} + \underset{base}{H_2O}$$

$$\underset{acid}{BF_3} + \underset{base}{NH_3} \rightarrow F_3B - NH_3$$

$$\underset{acid}{AlCl_3} + \underset{base}{NH_3} \rightarrow AlCl_3 \bullet NH_3$$

15.6 Buffers

A buffer is a solution made of an equal molar mixture of an acid and its conjugate base. It has the property that it stabilizes the pH to additions of acid or base. As an example consider acetic acid-acetate buffer. The equilibrium for acetic acid is

$$HOAc \rightarrow OAc^- + H^+ \qquad K_a = \frac{[H^+][OAc^-]}{[HOAc]} = 1.74 \times 10^{-5}$$

If we neglect the ionization of water we may write

$$[H^+] = \frac{[HOAc]}{[OAc^-]} K_a$$

and taking the negative log

$$pH = pK_a + log\,\frac{[HOAc]}{[OAc^-]}.$$

If we choose equimolar concentrations of acetic acid and acetate we get

$$pH = pK_a = 4.76$$

because $log\,1 = 0$.

The addition of extra H^+ will have little effect is there is excess $HOAc$ and OAc^- due to LeChatlier's principle.

15.6.1 Buffer Action in More Detail

Add 0.1M sodium acetate, NaOAc, to a solution 0.1M in acetic acid, HOAc. To this we may add X moles hydrochlroic acid, HCl (we are keeping the volume constant so that we may deal in concentration units). We know that

$$pH = pK_a - log\,\frac{[HOAc]}{[OAc^-]}.$$

Also from mass balance $0.1+0.1 = [HOAc]+[OAc^-]$, $[Na^+] = 0.1$ and $Cl^-] = X$. From charge balance $[H^+]+[Na^+] = [OH^-]+[OAc^-]+[Cl^-]$ or $[H^+]+0.1 = \frac{K_w}{[H^+]} + [OAc^-]+X$. Neglect the hydrolysis of water and solve for $[OAc^-] = 0.1 + [H^+] - X$ and for $[HOAc] = 0.2 - [OAc^-] = 0.1 - [H^+] + X$.

$$pH = pK_a - log\,\frac{0.1 - [H^+] + X}{0.1 + [H^+] - X} \approx pK_a - log\,\frac{0.1 + X}{0.1 - X}$$

This is constant for a range of values of X, the added acid from HCl.

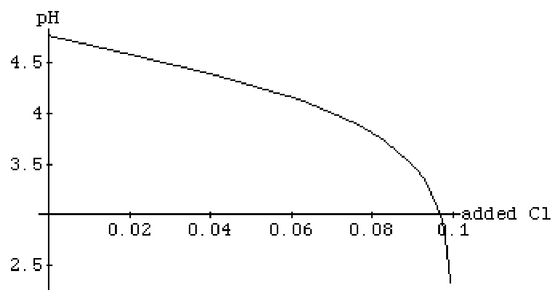

Figure 15.1: Adding Acid to a Buffer Solution

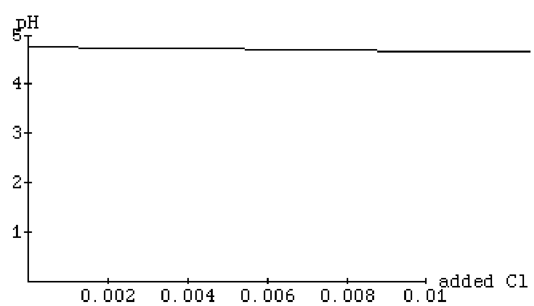

Figure 15.2: Adding Acid to a Buffer Solution Larger Scale

Adding acid to water in the absence of a buffer changes the pH:

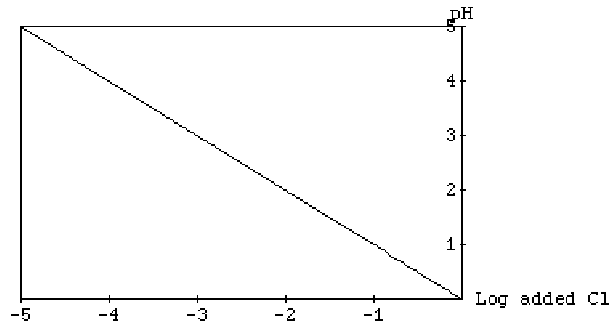

Figure 15.3: Adding Acid to Water

15.7 Hydrolysis

The conjugate base of a weak acid will neutralize water to form the weak acid Such a solution will have a basic pH. Consider a solution 0.1M in acetate.

$$OAc^- + H_2O \longrightarrow HOAc + OH^-$$
$$0.1 - x \quad x \quad x$$

or

$$x^2 \approx 0.1 \times K_h = \frac{K_w}{K_a} = 5.54 \times 10^{-10}$$

and since $[OH^-] = x$

$$pH = 14 - (-\,log\,x) = 8.87$$

15.8 Acid and Base Titration

In this discussion we will use a fixed amount of acid (a given concentration and volume) and neutralize it by the addition of aliquots of base at a given concentration. First we treat the case of the titration of a strong acid with a strong base and then the case of a weak acid-strong base titration.

15.8.1 Strong Acid-Strong Base

The concentration of base is C_b and its volume v_b while the concentration of the acid is C_a and volume v_a. Acid is neutralized by base according to

$$H^+ + OH^- \longrightarrow H_2O$$

and we may just assume neutralization of each amount of base added occurs. So if v_b mL of base is added to acid the number of moles of acid left is $v_a \times c_a - v_b \times c_b$ and the concentration of acid is

$$\frac{v_a \times c_a - v_b \times c_b}{v_a + v_b}$$

The pH is $pH = -\,log\, \frac{v_a \times c_a - v_b \times c_b}{v_a + v_b}$. In doing this we have ignored the hydrolysis of water. When we have added enough base to completely neutralize the acid the pH expression above looses its meaning and the pH $= -\,log\,\sqrt{K_w} = 7$.

Let us make an exact calculation. We are mixing HCl and NaOH in water. The unknowns are:

$$H^+,\ Cl^-,\ Na^+,\ OH^-$$
$$we\ need\ four\ equations:$$
$$mass\ balance$$
$$[Cl^-] = \frac{v_a \times c_a}{V}$$
$$[Na^+] = \frac{v_b \times c_b}{V}$$
$$hydrolysis\ of\ water$$
$$[OH^-] = \frac{K_w}{[H^+]}$$
$$charge\ balance$$
$$[H^+] + [Na^+] = [OH^-] + [Cl^-]$$
$$substituting$$
$$[H^+] + \frac{v_b \times c_b}{V} = \frac{K_w}{[H^+]} + \frac{v_a \times c_a}{V}$$

This is a quadratic equation whose solution is

$$[H^+] = \tfrac{1}{2}\left\{-\frac{c_b * v_b - c_a * v_a}{v_b + v_a} \pm \sqrt{(\frac{c_b * v_b - c_a * v_a}{v_b + v_a})^2 + 4K_w}\right\}$$

At the equivalence point $c_b * v_b - c_a * v_a = 0$ and $[H^+] = \frac{1}{2}\sqrt{4K_w}$. A plot of pH vs. v_b the added base gives the following curve.

15.8.2 Weak Acid vs. Strong Base

Using the example of the titration of acetic acid, $HOAc$, by OH^- let the concentration of base be C_b and its volume v_b and the concentration of the acid be C_a with volume v_a. The acid is neutralized by base according to

$$HOAc + OH^- \longrightarrow Ac^- + H_2O$$

The equilibrium constant expression for the dissociation of the weak acid is

$$AcOH + H_2O \longrightarrow AcO^- + H_3O^+ \qquad K_a = \frac{[Ac^-][H_3O^+]}{[AcOH]}$$

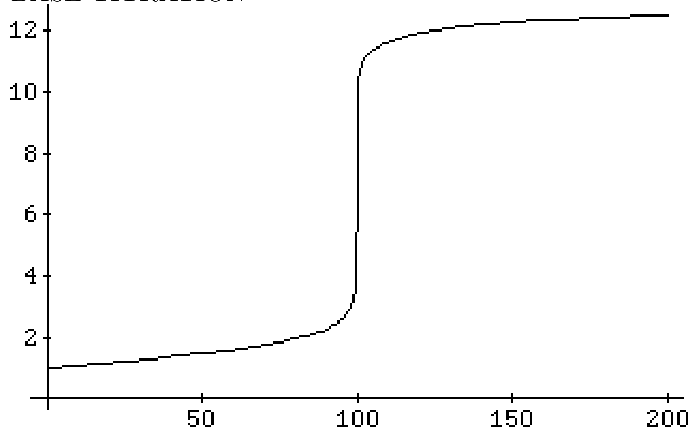

Figure 15.4: Titration of Strong Acid by a Strong Base

the equilibrium constant for water

$$H_2O \longrightarrow H^+ + OH^- \qquad K_w = [H^+][OH^-]$$

and the equilibium constant expression for the neutralization reaction

$$K_n = \frac{1}{K_h} = \frac{[Ac^-]}{[AcOH][HO^-]} = \frac{K_a}{K_w} = \frac{1}{5.54 \times 10^{-10}}$$

⋄At the start of the titration we have pure weak acid and the pH is given by

$$pH = -\,log\sqrt{K_a} = 2.87$$

⋄When enough neutralization has occured so that $[HOAc] = [OAC^-]$ the system is in the buffer region and the $pH = pK_a = 4.75$.

⋄The *equivalence point* is when we have added enough base equal to the number of moles of acid and have thus "neutralized" the acid. At this point the pH is governed by the hydrolysis of OAc^-.

$$\begin{array}{llll} OAc^- + H_2O \longrightarrow & HOAc + & OH^- & K_h = 5.54 \times 10^{-10} \\ \frac{c_a \times v_a}{v_a + v_b} - x & x & x & \end{array}$$

So,

$$x^2 = \{\frac{c_a \times v_a}{v_a + v_b} - x\}K_h \approx \{\frac{c_a \times v_a}{v_a + v_b}\}K_h$$

$$x = \sqrt{\{\frac{c_a \times v_a}{v_a + v_b}\}K_h}$$

$$and$$

$$pH = 14 + log\, x = 8.72$$

Now the "exact" method. The number of unknowns are $[Ac^-]; [AcOH]; [H^+]; [HO^-]$ and $[Na^+]$ and we must have five equations. We are balancing moles reacting, but we can easily express quantities in concentration units.

$$\begin{aligned}
&mass\ balance\ for Acetate\\
&[HOAc] + [OAc^-] = \frac{c_a \times v_a}{v_a + v_b}\\
&mass\ balance\ for\ sodium\\
&[Na^+] = \frac{c_b \times v_b}{v_a + v_b}\\
&charge\ balance\\
&[H^+] + [Na^+] = [OH^-] + [OAc^-]\\
&equilibrium\ constant\ expressions\\
&K_a = \frac{[Ac^-][H_3O^+]}{[AcOH]}\\
&K_w = [H^+][OH^-]
\end{aligned}$$

Using the [HOAc] mass balance equation and the equilibrium constant expression

$$[OAc^-] = c_a \times \frac{v_a}{v_a + v_b} - \frac{[OAc^-][H^+]}{K_a}$$

substituting into the charge balance equation gives

$$\begin{aligned}
&[H^+] + \frac{c_b \times v_b}{v_a + v_b} = \frac{K_w}{[H^+]} + \frac{v_a}{v_a + v_b}\frac{K_a}{[H^+] + K_a}\\
&[H^+]^2 + \left(K_a + \frac{c_b \times v_b}{v_a + v_b}\right)[H^+] - \frac{K_a K_w}{[H^+]} + K_a\left(\frac{c_b \times v_b}{v_a + v_b} - \frac{c_a \times v_a}{v_a + v_b}\right) - K_w = 0
\end{aligned}$$

Solving for $[H^+]$ the plot of pH vs. v_b give the following curve.

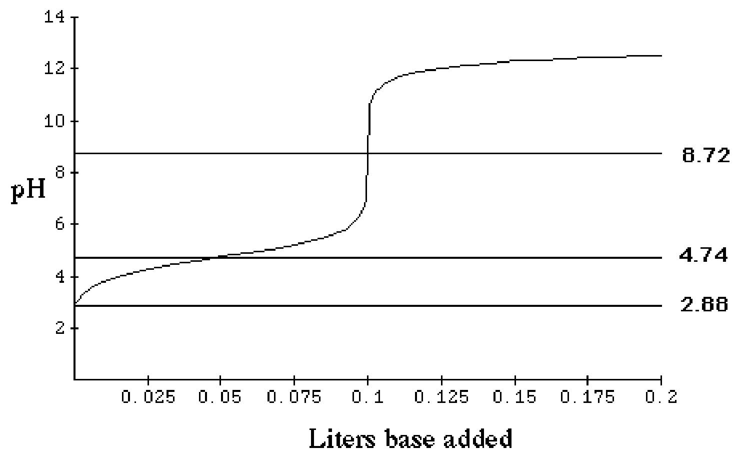

Figure 15.5: Titration of Weak Acid by a Strong Base