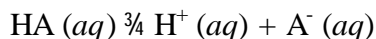


Weak acids and bases

Weak Acids

Equilibrium

All weak acids in solution exist in equilibrium. The equilibrium is between the molecular form of the acid and the ionized form of the acid.



For all weak acids this equilibrium lies predominantly on the left. Most of the acid is in the molecular form. This results in all weak acids having an equilibrium constant that is less than 1. The largest equilibrium constant is approximately 10^{-2} . The smallest is about 10^{-13} . The equilibrium expression for all monoprotic weak acids is

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

where K_a is the acid-ionization constant.

Determination of K_a

K_a can be determined in a variety of ways. The most common is by measuring the pH of a solution of the weak acid in question. This method works fine for monoprotic acids, but for polyprotic acids, the result is a combination of the various K 's for each acidic proton. Titration is a method that works well for either monoprotic or polyprotic acids. Measuring the pH at various points in the titration and plotting the pH vs. the volume of the base added gives an indication of the K 's for the acid.

Examples

A 0.10 M weak acid has a pH of 4.56. What is the K_a for the acid?

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-4.56} = 2.8 \times 10^{-5} \text{ M}$$

| | | | |
|------------|----------|----------------|----------------|
| | HA | H ⁺ | A ⁻ |
| Initial [] | 0.10 | 10^{-7} | 0 |
| Δ | -x | +x | +x |
| Final [] | 0.10 - x | $10^{-7} + x$ | x |

$(10^{-7} + x)$ is the equilibrium hydrogen ion concentration which is 2.8×10^{-5} M. This is also equal to the $[\text{A}^-]$ due to the stoichiometry of the problem. The $[\text{HA}]$

at equilibrium is essentially the same as it was at the beginning. This gives a K_a of

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(2.8 \times 10^{-5})^2}{0.10} = 7.6 \times 10^{-9}$$

This acid is a fairly weak acid.

Using K_a

The use of K_a is just like the use of any other equilibrium constant. We can use it to find the equilibrium concentrations of everything in the solution or just one thing, usually Hydrogen ion. The methods of solving a weak acid (or weak base) equilibrium are the same as for any other type of equilibrium. Usually we are able to make some approximations to the problem that makes the mathematics easier to solve. Sometimes, we just have to work our way through the (usually) quadratic equation that comes up. The thing to remember about this is that these are still equilibrium problems. They are no different than any other equilibrium problem we have done before.

Examples

Calculate the pH of a 0.15 M solution of Acetic acid. $K_a = 1.8 \times 10^{-5}$.

Set up the problem the same way.

| | | | |
|------------|-----------------------------------|---------------|------------------------------------|
| | $\text{HC}_2\text{H}_3\text{O}_2$ | H^+ | $\text{C}_2\text{H}_3\text{O}_2^-$ |
| Initial [] | 0.15 | 10^{-7} | 0 |
| Δ | -x | +x | +x |
| Final [] | $0.15 - x$ | $10^{-7} + x$ | x |

This gives an equilibrium expression that looks like

$$K_a = \frac{[10^{-7} + x][x]}{[0.15 - x]} = 1.8 \times 10^{-5}$$

The quantity we are looking for is $10^{-7} + x$. We can make some guesses at approximation though. For instance, x is probably pretty small since this is a weak acid. Therefore, we can probably ignore it in comparison to 0.15. Also, it is an acid so the amount of Hydrogen ion produced is likely to be much larger than the amount from the auto-dissociation of water so we can ignore the 10^{-7} in relation to x. This gives a simplified equilibrium expression that looks like

$$K_a = \frac{[x][x]}{[0.15]} = 1.8 \times 10^{-5}$$

This can be solved relatively (compared to the full quadratic) easily.

$$K_a \approx \frac{[x][x]}{[0.15]} \approx 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.15} \approx 1.8 \times 10^{-5}$$

$$x^2 \approx 1.8 \times 10^{-5} \times 0.15 = 2.7 \times 10^{-6}$$

$$x \approx \sqrt{2.7 \times 10^{-6}} = 1.6 \times 10^{-3} \approx [H^+]$$

Now we need to check our assumptions. Is this value much less than 0.15? If we subtract this from 0.15 we get 0.1484, which within the significant figures of the problem is essentially 0.15. What about the assumption that it is much larger than 10^{-7} ? This value plus 10^{-7} is 1.6001×10^{-3} . Again, within the significant figures of the problem, this is 1.6×10^{-3} . We can now use this value to calculate the pH which is

$$pH = -\log[H^+] = -\log(1.6 \times 10^{-3}) = 2.80$$

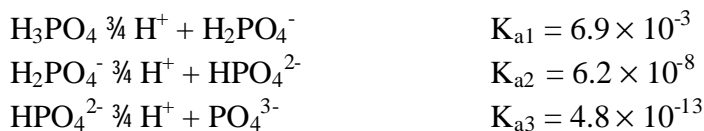
Polyprotic acids

Most polyprotic acids are weak. The exception is the first proton to come off Sulfuric acid, which is strong. A polyprotic acid has a K_a for each acidic proton on the acid. Each successive K_a is smaller than the previous one. The reason for this is explained in Chapter 15. Given that there is more than one place for the protons to enter the solution, how do we handle the calculation of the pH of such a solution? The answer is easier than one would think. We can handle each of the proton ionizations as separate problems. The results from the previous one are the initial concentrations for the next.

Example

What is the pH of a 0.10 M Phosphoric acid solution?

The three equilibria are.



We solve the first equilibrium. If we use the quadratic equation to solve this problem, we get $[H^+] = [H_2PO_4^-] = 0.023$. This then becomes the initial conditions for the second ionization.

| | $H_2PO_4^-$ | H^+ | HPO_4^{2-} |
|------------|-------------|-----------|--------------|
| Initial [] | 0.023 | 0.023 | 0 |
| Δ | -x | +x | +x |
| Final [] | 0.023 - x | 0.023 + x | x |

If we make some simplifying assumptions here, which are valid, we get that the Hydrogen ion concentration is the same as it is from the first ionization. The concentration of the HPO_4^{2-} ion is equal to K_{a2} . These then become the initial conditions for the third ionization.

| | HPO_4^{2-} | H^+ | PO_4^{3-} |
|------------|--------------|-----------|-------------|
| Initial [] | K_{a2} | 0.023 | 0 |
| Δ | -x | +x | +x |
| Final [] | $K_{a2} - x$ | 0.023 + x | x |

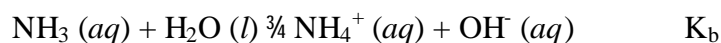
Solving this problem using the simplifying approximations gives that the Hydrogen ion and monohydrogen phosphate ion concentrations do not change significantly. The concentration of the phosphate ion is

$$[PO_4^{3-}] = \frac{K_{a3}K_{a2}}{[H^+]}$$

These results will be the same for any triprotic weak acid.

Weak Bases

Weak bases are almost always derivatives of the Ammonia molecule (NH_3). Weak bases in water undergo **hydrolysis**, the breaking apart of water.



The equilibrium expression for this is

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

K_b is called the **base-ionization constant**. The methods for determining K_b are the same as those used to determine K_a . K_b can also be used to determine the pH of a solution of a weak base. There are no polyprotic weak bases that we are going to look at.

Example

Calculate the pH of a 0.25 M pyridine solution. $K_b = 1.4 \times 10^{-9}$.

Set up the problem the way we would for any equilibrium.

| | Py + | H ₂ O $\frac{3}{4}$ | PyH ⁺ + | OH ⁻ |
|---------------|---------|--------------------------------|-----------------------|-----------------|
| Initial [] | 0.25 | | 0 | 10^{-7} |
| Δ | -x | | +x | +x |
| Final [] | 0.25-x | | x | $10^{-7}+x$ |

$$K_b = \frac{[PyH^+][OH^-]}{[Py]} = \frac{(x)(10^{-7} + x)}{0.25 - x}$$

We can try our assumptions here too.

$$K_b = \frac{[PyH^+][OH^-]}{[Py]} = \frac{(x)(10^{-7} + x)}{0.25 - x} \approx \frac{x^2}{0.25} \approx 1.4 \times 10^{-9}$$
$$x \approx \sqrt{(0.25)(1.4 \times 10^{-9})} = 1.9 \times 10^{-5} \approx [OH^-]$$

Are the approximations valid? This value is approximately the same as itself plus 10^{-7} . Also it is much less than the value of 0.25, so the approximations are valid. The pH can now be calculated. First find the Hydrogen ion concentration.

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.9 \times 10^{-5}} = 5.3 \times 10^{-10}$$
$$pH = -\log(5.3 \times 10^{-10}) = 9.27$$

pH of a salt solution

To determine the pH of a salt solution, we must first look at the ions that make up the salt.

- If both ions come from a strong acid and base then the pH of the solution of that salt will be neutral (7.0).
- If one of the ions comes from a weak acid, the pH will be basic (>7.0) because the conjugate of the weak acid will be a weak base, which will hydrolyze and produce Hydroxide ions.

- If one of the ions comes from a weak base, the pH will be acidic (<7.0) because the conjugate of a weak base is a weak acid. The weak acid will dissociate, producing Hydrogen ions.
- If the ions come from both a weak acid and a weak base, the pH can be determined by finding which of the conjugates is stronger. If the conjugate acid is stronger the solution will be acidic. If the conjugate base is stronger the solution will be basic.

Buffers

A solution that contains significant amounts of both a weak acid and its conjugate base (or vice versa) **before** equilibrium is reached is a **buffer**. A buffer is a solution that will resist a change in pH upon the addition of acid or base. This works because, in the solution, there is a significant amount of acid and base present to react with any base or acid that is added. This keeps the equilibrium at approximately the same point, keeping the pH relatively constant.

If we are able to make some simplifying assumptions in the equilibrium calculation, we can find a simple relationship between the pH of a buffer solution and the ratio of the acid to its conjugate base. The relationship is dependent on the equilibrium constant for the acid in question.

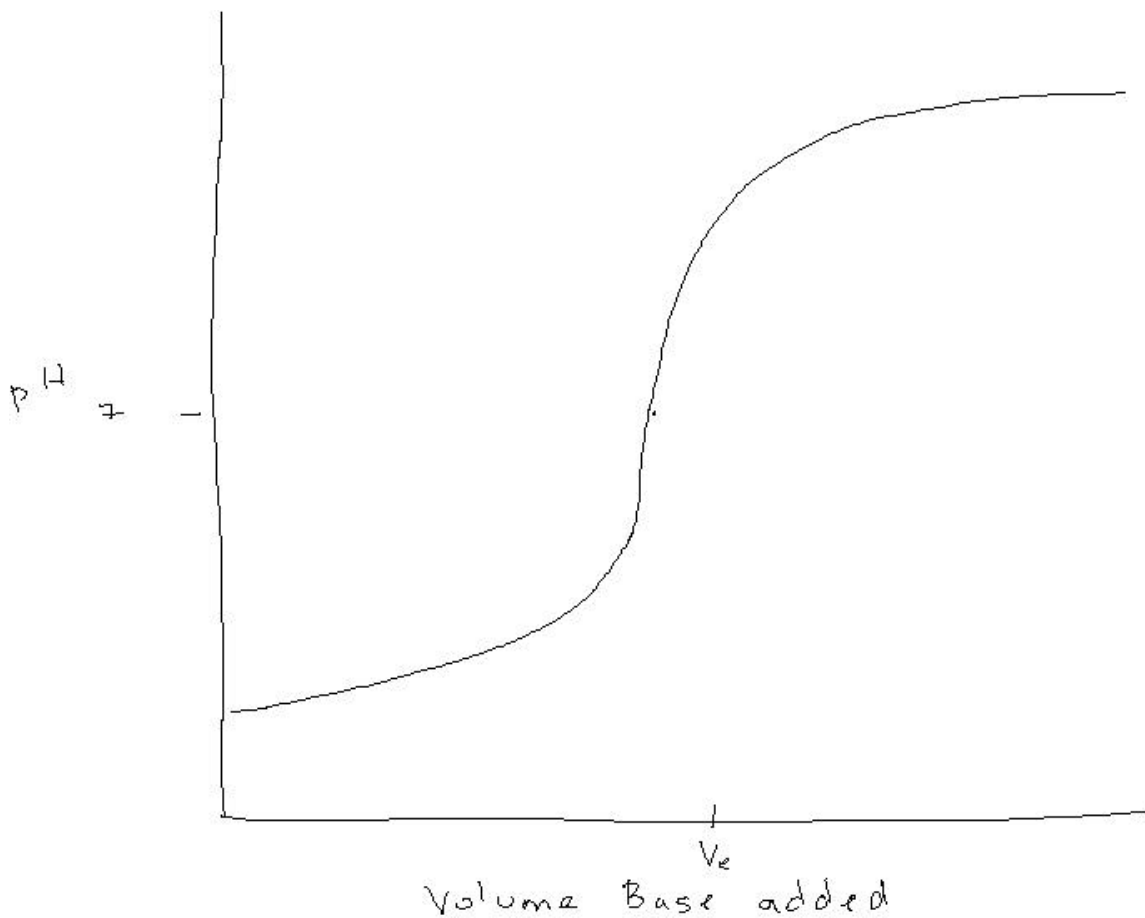
$$pH = pK_a + \log \frac{[base]}{[acid]}$$

This equation is known as the **Henderson-Hasselbalch** equation. pK_a is the negative of the common logarithm of the K_a . This relationship will hold if there is a buffer present. This is a simplification of the equilibrium calculation. Using this equation or the full quadratic in the equilibrium calculation should give the same results.

Titration Curves

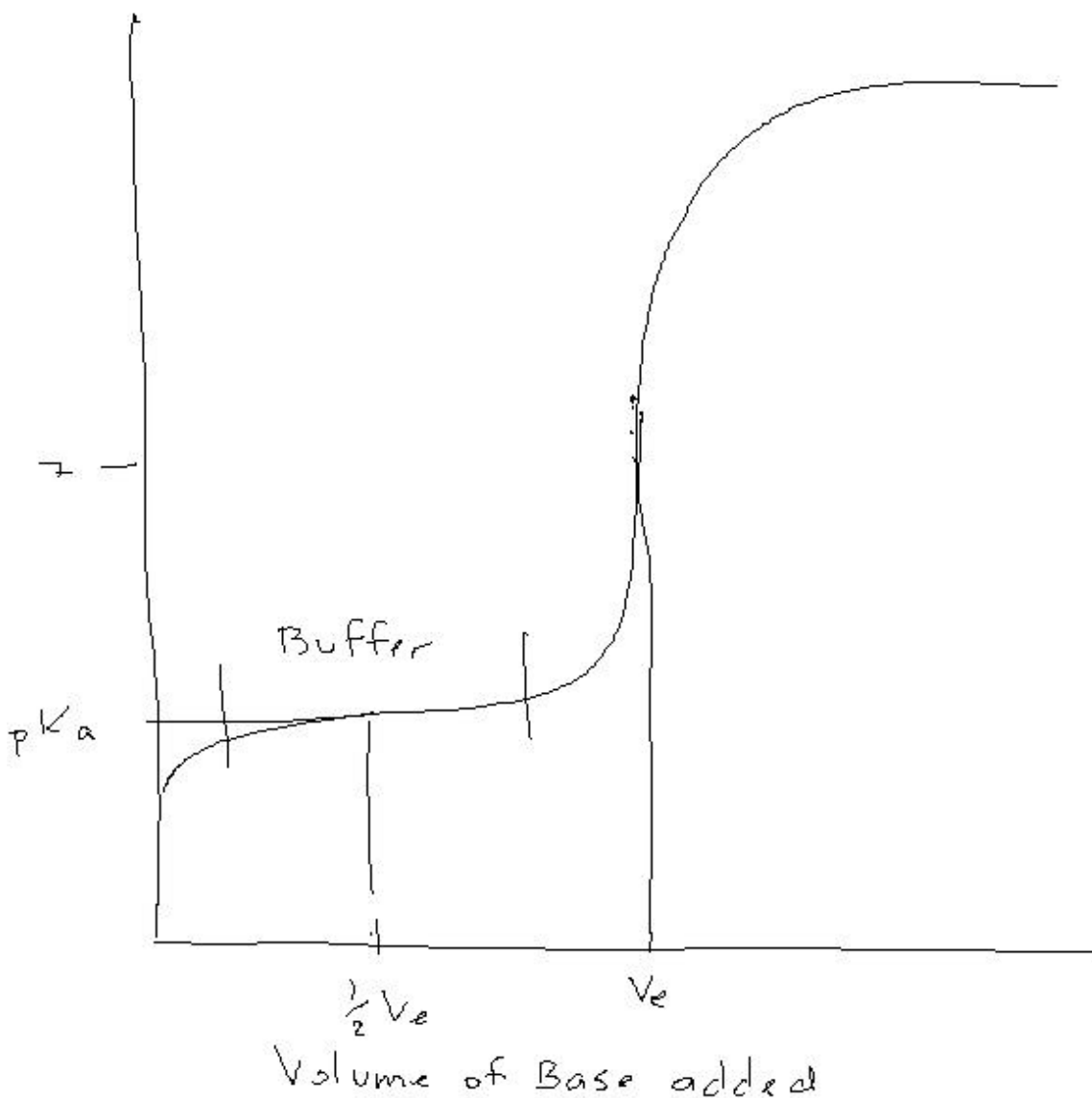
Strong acid – Strong base

This curve is relatively simple. The pH starts at the pH of the strong solution. The pH of the end-point is always 7.0. The calculations involved are simple stoichiometry calculations.



Weak acid – Strong base

This curve is a little more interesting. The pH starts at the pH of the weak acid. The pH at the end-point will always be above 7.0. The calculations involved here are the stoichiometry and the equilibrium calculations we have been doing in this chapter. Most of the way up to the end-point a buffer is present so the calculations there will involve the Henderson-Hasselbalch equation. At the point where the volume of base added is halfway to the end-point, the pH of the solution is equal to the pK_a of the weak acid.



Weak base – Strong acid

This curve is similar to the curve above. The pH starts at the pH of the weak base. The pH at the end-point here will always be below 7.0. Most of the way up to the end-point a buffer is present so the calculations there will involve the Henderson-Hasselbalch equation. At the point where the volume of base added is halfway to the end-point, the pH of the solution is equal to the pK_a of the conjugate acid of the weak base.

