Chapter 8, Acid-base equilibria

Road map of acid-base equilibria

On first encounter, the study of acid-base equilibria is a little like a strange land with seemingly confusing trails that make passage difficult. In fact, there is a road map that, once understood, allows us to navigate acid-base equilibria with confident precision and so become masters of its domain. Here is an overview of this road map.

Fundamentally, aqueous acid-base equilibria are just a particular example of the ideas and techniques we have already learned in the study of gas phase chemical equilibria. However, there are two aspects that complicate the application of these ideas. First, because the autoionization of water,

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq),\ K_w,$$

is always present in aqueous solution, the analysis of aqueous acid-base equilibria must always take into account at least two *competing equilibria*, the acid or base ionization and the water autoionization. Second, because we will be interested in how acid-base equilibria respond to changes in the system (typically by adding additional base or acid), we need also to be able to separate the chemical reactions that take place when things are combined from the subsequent equilibration of the reaction product. The key idea is to let what are combined react 100% as a *limiting reagent problem* as a preliminary step done *before* equilibration.

Our overarching goal, then, is to learn to clearly distinguish and to separately master these two aspects—competing equilibria and limiting reagent reactions. Once this is achieved, we will have a framework in which any problem in aqueous acid-base equilibria can be solved in a straightforward way.

The approach we take is to distinguish four *regimes*:

1. pure acid (or base) solution,
2. acid (or base) that has been partially consumed by addition of base (or acid),
3. acid (or base) that has been exactly consumed by addition of base (or acid),
4. acid (or base) that has been consumed by reaction with excess base (or acid).

The details will be different depending on whether the acid (or base) initially present is a weak or strong acid (or base), that is, whether its ionization constant is large or small compared with 1. In all cases, the other component will be a strong base (or acid).

The first regime is a straightforward equilibrium problem. The second regime involves reaction of the acid and base as a limiting reagent problem, followed by straightforward equilibration of the resulting solution. The third regime is handled differently depending on whether the acid (or base) initially present is a weak or strong acid (or base). The fourth regime, like the second, involves reaction of the acid and base as a limiting reagent problem, but then equilibration of the products is simple since it will always be the excess base (or acid) that is left after the limiting reagent reaction.

You will know that you have mastered this road map of acid-base equilibria when you approach such an equilibrium as a two step process: First (always!), determine *which regime applies*. Then, implement the calculational procedure for that regime to *determine the chemical equilibrium*. That really is all there is to it. In this way you can come to find that things will seem simple; not easy, but simple.

So, our plan is to learn about each of the four different regimes. We'll do this for each one in turn. Then we'll see how to put everything together, to construct a *titration curve*—the variation of pH throughout the four regimes. Finally, we'll construct a compact summary of the road map.

So let's begin, by defining just what acid-base reactions are and how to characterize them.

Acid-base reactions

We are going to be working with acid-base equilibria in aqueous solution, and we will use the Brønsted-Lowry definitions that an acid is a source of H^+ and a base is an acceptor of H^+.

■ Acid ionization constant K_a

A convenient way to write the reaction of an acid HA in water is

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq).$$

Here water is acting as a base, accepting the H^+; the result, H_3O^+, called the *conjugate acid* of H_2O, since H_3O^+ can donate H^+ to reform H_2O. In a similar way, A^- is called the *conjugate base* of the acid HA, since A^- can accept H^+ to reform HA. The equilibrium constant is known as the *acid ionization constant* K_a,

$$K_a = \frac{([\mathrm{H_3O^+}]/1\,\mathrm{M})\,([\mathrm{A^-}]/1\,\mathrm{M})}{([\mathrm{HA}]/1\,\mathrm{M})},$$

where the reference concentration, 1 M, is written explicitly; liquid water does not appear, because its reference concentration is just the liquid water, so its activity is 1. (Strictly, we are assuming that solutes are sufficiently dilute that the concentration of the water is negligibly affected by their presence.) Usually, we will abbreviate K_a as

$$K_a = \frac{[\mathrm{H_3O^+}]\,[\mathrm{A^-}]}{[\mathrm{HA}]},$$

with the understanding that […] stands for the numerical value—without units—of the concentration in mol/L. As usual, K_a is unit-less.

An example acid ionization is

$$\mathrm{CH_3COOH}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3COO^-}(aq),$$

$$K_a = \frac{[\mathrm{H_3O^+}]\,[\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]}.$$

If K_a is much greater than 1, the acid is mostly dissociated and so is said to be a *strong acid*. If K_a is much less than 1, the acid is dissociated only to a small extent and so is said to be a *weak acid*.

■ Base ionization constant K_b

Similarly, we can write the reaction of a base B in water as

$$H_2O(l) + B(aq) \rightleftharpoons HB^+(aq) + OH^-(aq).$$

Here water is acting as an acid, donating the H^+; the result, OH^-, is called the *conjugate base* of H_2O, since OH^- can accept H^+ to reform H_2O. Analogously, HB^+ is called the *conjugate acid* of the base B, since HB^+ can donate H^+ to reform B. The equilibrium constant is known as the *base ionization constant* K_b,

$$K_b = \frac{[HB^+]\,[OH^-]}{[B]}.,$$

where we have used the abbreviated form.

Here is an example base ionization,

$$H_2O(l) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq),$$

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

If K_b is much greater than 1, the base reacts nearly completely with water and so is said to be a *strong base*. If K_b is much less than 1, the base reacts hardly at all with water and so is said to be a *weak base*.

■ Water autoionization constant K_w

In this analysis of acid and base ionization we see that water in one case plays the role of a base and the other plays the role of an acid. Indeed, the role that water plays in an aqueous equilibrium can be used as another definition of acid or base. A consequence of this dual role of water is that its equilibrium with H_3O^+ and OH^- is the reference standard against which aqueous acidity and basicity are defined.

Here is how this works. A general base ionization reaction is

$$H_2O(l) + B(aq) \rightleftharpoons HB^+(aq) + OH^-(aq),\ K_b,$$

and the ionization reaction of its conjugate acid is

$$HB^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + B(aq),\ K_a.$$

The sum of these two reactions is

$$2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq),\ K_w.$$

This equation is called the *autoionization* of water and its equilibrium constant is known as the *water autoionization constant* K_w. At 25°C it is equal to

$$K_w = [H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}$$

Now, we have seen that the equilibrium constant of a sum of two reactions is the product of the equilibrium constants of the summed reactions. Therefore, we know that water autoionization constant can be expressed as

$$K_w = K_a\,K_b.$$

This means we can compute the base ionization constant from the ionization constant of its conjugate acid,

$$K_b = K_w / K_a = 10^{-14} / K_a ,$$

where the last equality is for 25°C. It is for this reason that base ionization constants are generally not tabulated.

■ pH

Because K_w is so small, water is ionized only very slightly. We can compute the concentration of H_3O^+ and OH^- by solving the autoionization equilibrium.

	$[H_3O^+]/M$	$[OH^-]/M$
initial	0	0
equilibrium	x	x

Initial and equilibrium activities for the autoionization of liquid water.

The equilibrium expression is then

$$K_w = 1. \times 10^{-14} = x^2$$

and so the concentration of H_3O^+ and OH^- are each 1×10^{-7} M at 25°C.

Now, as we will see in a moment, strong acids can have H_3O^+ concentrations of 1 M or more. This means that H_3O^+ varies over many powers of 10 (orders of magnitude), and so it is convenient to measure $[H_3O^+]$ on a *logarithmic scale*. Also, for weak acids and bases, which is what we will be interested in primarily, concentrations of H_3O^+ and OH^- are generally much less than 1 M, which means their logarithms are negative, and so it is more convenient to work with the *negative logarithms* so that we have a positive quantity.

For this reason, the notation *pAnything* is defined as

$$\text{pAnything} = -\log_{10}(\text{Anything})$$

and in particular pH and pOH are defined as

$$\text{pH} = -\log_{10}([H_3O^+]/1\,\text{M}) = -\log_{10}([H_3O^+]),$$

$$\text{pOH} = -\log_{10}([OH^-]/1\,\text{M}) = -\log_{10}([OH^-]),$$

where in each case the second equality is written with understanding that […] stands for the numerical value—without units—of the concentration in mol/L.

> Show that pure water at 25°C has $\text{pH} = \text{pOH} = 7$.

> To get a feeling for the amounts involved, how many OH^- ions are present in 1 liter of pure water at 25°C? How many H_2O molecules are present? The molecules and ions present in water are constantly buffeting one another. On average, how many collisions does a water molecule make before it encounters an hydroxide ion?

Since acids produce additional H_3O^+, their pH is always less than 7. Similarly, since bases produce additional OH^-, their pOH is always less than 7. We can relate pH and pOH, by calculating pK_w.

$$\begin{aligned} pK_w & \\ &= -\log_{10}(K_w) \\ &= -\log_{10}([H_3O^+][OH^-]) \\ &= -\{\log_{10}([H_3O^+]) + \log_{10}([OH^-])\} \\ &= -\log_{10}([H_3O^+]) - \log_{10}([OH^-]) \\ &= pH + pOH \end{aligned}$$

This means that at 25°C

$$pH = 14 - pOH.$$

so that bases have pH greater than 7, at 25°C.

> Calculate the pH and pOH of the following HCl solutions, assuming the HCl dissociates 100%: 15 M, 10 M, 5 M, 1 M, 0.1 M and 0.01 M. Can pH be less than 0?

> Calculate the pH and pOH of the following NAOH solutions, assuming the NaOH dissociates 100%: 15 M, 10 M, 5 M, 1 M, 0.1 M and 0.01 M. Can pH be greater than 14?

It is important always to be mindful of the temperature being used. The reason is that equilibrium constants in general, and the value of K_w in particular, are different at different temperatures. This means that the pH of pure water will be different at different temperatures. For this reason, saying a solution has pH = 7 does *not*, by itself, mean the solution is "neutral" (has equal concentrations of H_3O^+ and OH^-. More generally, the acidic or basic character of a solution is due to the *relative concentrations* of H_3O^+ and OH^-, rather than a particular numerical value of pH.

> Like all equilibrium constants, the autoionization constant of water changes with temperature. At 10°C its value is 0.292×10^{-14} and at 30°C its value is 1.47×10^{-14}. Calculate the pH and pOH of water at 10°C and 30°C. Based on your results, does the "acidity" of water depend on temperature?

> Use the dependence the values of the equilibrium constants in the previous problem to estimate the standard enthalpy change and the standard entropy change of the water autoionization reaction.

■ Origin of the notation pH

Several years ago a student asked where the notation "p" came from. Another student answered that it was from the French word *pouvoir* (in this sense, capability), referring to the power of ten. I asked a French-speaking colleague about this, and her response was that perhaps it was from the French word *puissance* (power) instead. Eventually we checked the *Oxford English Dictionary, 2e*. Here is what it says:

> "Introduced (in Ger.) as pH, by S. P. L. Sörensen 1909, in Biochem. Zeitschr. XXI. 134, the p repr. G. potenz power and H the hydrogen ion."

That is, it is from the German (!) word *potenz* (power). So, the next question is, can we get a reference tracing an earlier French use? That way we could decide which use takes precedence.

Now that we have seen what acid-base reactions are and how to characterize them, let's follow our road map to study these reactions in their four different regimes.

Regime 1: pure strong acid (or base)

HCl is a strong acid, with $K_a = 10^7$. What is the pH of 10 M HCl?

We can begin as usual by setting up the equilibrium. The ionization reaction is

$$\mathrm{HCl}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq).$$

The equilibration analysis is

	$[HCl]/M$	$[H_3O^+]/M$	$[Cl^-]/M$
initial	10.	$1. \times 10^{-7}$	0.
equilibrium	$10. - 1.\,x$	$1. \times 10^{-7} + x$	x

Initial and equilibrium activities for the aqueous ionization of 1 M HCl.

Now, because K_a is so large, at equilibrium the HCl will be nearly 100% ionized. This means that x is very large. In a case such as this we have learned that it makes sense to use revised initial conditions, starting from 100% ionized acid.

	$[HCl]/M$	$[H_3O^+]/M$	$[Cl^-]/M$
initial	10.	$1. \times 10^{-7}$	0.
revised initial	0.	10.	10.
equilibrium	y	$10. - 1.\,y$	$10. - 1.\,y$

Initial, revised initial and equilibrium activities for the aqueous ionization of 1 M HCl.

Here we have included the contribution 10^{-7} M H_3O^+, due to the autoionization of water, but this is negligible compared to the 10 M H_3O^+ from the 10 M HCl. The resulting equilibrium expression is

$$K_a = 10^7 = \frac{(10 - y)^2}{y}.$$

Now, since $K_a \gg 1$, most of the HCl is ionized, the change y to achieve equilibrium is small. This means that $10 - y$ is negligibly different from 10, and so we can approximate the equilibrium constant expression as

$$K_a = 10^7 \approx \frac{10^2}{y}.$$

so that $y = 1 \times 10^{-5}$.

> Confirm this result.

Show that the percent of 10. M HCl that is *undissociated* is 1×10^{-4}, that is, that 10 M HCl becomes 99.9999 % dissociated.

The net result of all of this is that *the molarity of H_3O^+ is the same as the nominal (that is, ignoring any dissociation) molarity of the HCl*. Thus, the pH of 10 M HCl is

$$\mathrm{pH} = -\log_{10}(10) = -1$$

This is a general result for strong acids, so that in such cases we can immediately calculate the pH as $-\log_{10}$(molarity). The pOH is

$$\text{pOH} = 14 - \text{pH} = 14 - (-1) = 15.$$

This means that at 25°C the concentration of OH^- in 10 M HCl is 10^{-15} M!

> How many undissociated HCl molecules are present in 1 liter of 10 M HCl at 25°C? How many chloride ions are present? The molecules and ions present in 10 M HCl are constantly buffeting one another. On average, how many collisions does a water molecule make before it encounters an HCl molecule? On average, how many collisions does a chloride ion make before it encounters an hydronium ion?

> Calculate the pH and pOH of 0.1 M HCl at 25°C.

Here is another example. At 25°C a strong acid, HA, has ionization constant $K_a = 10^4$.

> State whether $\Delta G°$ is greater than zero, zero, or less than zero. Justify your answer.

> Calculate the concentration of H_3O^+ in a 10 M aqueous solution of HA at 25°C.

> Calculate the pH of a 10 M aqueous solution of HA at 25°C.

> Calculate the concentration of undissociatedHA in a 10 M aqueous solution of HA at 25°C.

Since $K_a \gg 1$, this means that if 1 M each of HA, H_3O^+ and A^- are combined, then spontaneously most of the HA will react with water to form additional H_3O^+ and A^-. That is, relative to standard states, the acid ionization is spontaneous and so $\Delta G° < 0$.

To answer the other three questions, we need to set up the acid ionization equilibrium. Since $K_a \gg 1$, we'll do this by assuming first that all of the acid ionizes.

	$[HA]/M$	$[H_3O^+]/M$	$[A^-]/M$
initial	10	1×10^{-7}	0
revised initial	0	$10 + 10^{-7} \approx 10$	10
equilibrium	y	$10 - y \approx 10$	$10 - y \approx 10$

This analysis shows that the equilibrium concentration of H_3O^+ is 10 M and so the pH is $-\log(10) = -1$. It also shows that the concentration of undissociated HA at equilibrium is the value of y. We get this from the equilibrium constant expression,

$$K_a = 10^4 = \frac{(10 - y)^2}{y} \approx \frac{10^2}{y} \to y = \frac{10^2}{10^4} = 10^{-2}.$$

This means the concentration of undissociated HA is 10^{-2} M.

Regime 1: pure weak acid (or base)

We have seen that the hydronium ion concentration in pure water (at 25°C) is 10^{-7} M. When an acid dissolves in water, it donates additional hydronium ions and so their concentration rises above 10^{-7} M. Strong acids donate essentially all of their hydrogen to the solution in this way, because they are *nearly 100 % dissociated* (their K_a is much greater than 1). We showed this explicitly for the example of 10 M HCl.

Weak acids, on the other hand, only donate a small portion of their hydrogen ions to the solution. This is because the K_a of a weak acid is much less than 1, and so a weak acid is *mostly undissociated*. This means that, while the hydronium ion concentration of a weak acid is greater than 10^{-7} M, it is much less than that of an equivalent amount of strong acid.

■ Pure weak acid example

Here is how to calculate the hydronium ion concentration of a weak acid. As example, let's work with 1.712 M acetic acid, which we'll write simply as HA. The acid ionization is

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

and $K_a = 1.76\times10^{-5}$. We begin by assuming that initially no dissociation occurs, so that $[\mathrm{HA}] = c_a = 1.712$ M and $[\mathrm{A^-}] = c_b = 0$. The initial $[\mathrm{H_3O^+}] = 10^{-7}$, due to the autoionization of water. Because c_b is 0, the reaction quotient is $Q = 0$, which is less than K_a. This means that initially we have too much reactants, not enough products. Therefore, at equilibrium we must decrease the undissociated acid concentration to $c_a - x$, and so increase the conjugate base concentration from 0 to x, and increase the hydronium ion concentration from its value in pure water to $10^{-7} + x$. The amount of dissociation, x, is determined by solving the equilibrium expression

$$K_a = 1.76\times10^{-5} = \frac{(10^{-7}+x)\,x}{c_a - x} = \frac{(10^{-7}+x)\,x}{1.712 - x}.$$

We can simplify this equation by making two approximations. First, because K_a is much larger than the autoionization constant of water, K_w, we know that the hydronium ion concentration x contributed by the acid dissociation is *greater than* 10^{-7}. This in turn means that x is *not negligible compared to* 10^{-7}. We will assume, in fact, that x is s*o much greater than* 10^{-7} that we can ignore 10^{-7} relative to x,

$$10^{-7} + x \approx x.$$

Second, because K_a is much less than 1, HA dissociates only to a small extent. This means x is small compared to the initial concentration of the acid, c_a. We will assume, in fact, that x is s*o much smaller than* c_a that we can ignore x relative to c_a,

$$c_a - x \approx c_a.$$

Notice that in one case we are neglecting something compared to x, and in the other case we are neglecting x compared to something!

With these two approximations, the equilibrium expression becomes

$$K_a = 1.76\times10^{-5} = \frac{(10^{-7}+x)\,x}{c_a - x} = \frac{x^2}{c_a},$$

which we can solve by taking the square root to get

$$x = \sqrt{c_a K_a}\,.$$

> Use the values of K_a and c_a to show that $x = 5.49\times10^{-3}$.

This result shows that both of our approximations are justified: 5.49×10^{-3} is indeed large compared to 10^{-7}, but 5.49×10^{-3} is also small compared with 1.712. Always be sure to check to see that this is so.

> Show that the corresponding pH is 2.260.

> How many undissociated acetic acid molecules are present in 1 liter of 1.712 M acetic acid at 25°C? How many acetate ions are present? On average, how many collisions does an acetate ion make before it encounters a hydronium ion?

> Calculate the pH of 0.100 M acetic acid at 25°C. Besure to include the correct number of siginifcant figures in your answer.

> Compare the ratio of acetate ions to undissociated acetic acid at 25°C that are present in a 1.712 M solution and in a 0.100 M solution. Should the ratios be different? If the ratios differ, could you have predicted which of the ratios would be larger without doing any computations?

■ Pure weak base example

The same kind of analysis works for a weak base. Now the ionization reaction is

$$H_2O(l) + B(aq) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

and the equilibrium expression is

$$K_b = \frac{x(10^{-7} + x)}{c_b - x}$$

Since (we assume) K_b is greater than K_w, the hydroxide concentration, $10^{-7} + x$, is greater than 10^{-7}, and so x is *not negligible compare to* 10^{-7}. As before, we assume that x is in fact so much larger than 10^{-7} then we can ignore the 10^{-7}. But also, since (we assume) the base is weak, so that K_b is less than 1, it reacts with water only to a small extent, and so x is small compared to c_b. The result is that the equilibrium expression becomes

$$K_b = \frac{x(10^{-7} + x)}{c_b - x} \approx \frac{x^2}{c_b}$$

which we can solve by taking the square root to get

$$x = \sqrt{c_b K_b}\,.$$

For example, the K_b of NH_3 is 1.8×10^{-5}. We get this value from the K_a of the conjugate acid, NH_4^+, which is 5.6×10^{-10}.

> Show that $K_b = 1.8 \times 10^{-5}$.

> Show that a 0.112 M solution of NH_3 has hydroxide ion molarity $x = 1.41 \times 10^{-3}$.

As before, this value of x shows that the approximations are justified.

> Show that the pH is 11.15.

Regime 3: Neutralized weak acid (or base): hydrolysis

If we know the volume and molarity of a weak acid (or base), we can compute how many moles of the acid (or base) we have. If we add an amount of a strong base (or acid) that has the same number of moles, then we will exactly neutralize the weak acid (or base). The resulting solution will contain the conjugate base of the acid and the conjugate acid of the base. For example, if we neutralize acetic acid with sodium hydroxide, we will end up with a solution of acetate ions (the conjugate base of the acetic acid), water, (the conjugate acid of the hydroxide), and sodium ions—a solution of the salt sodium acetate.

The surprising thing is that the pH is such solutions is *not 7*. Here is why. Because the acid HA is weak, its conjugate base, A^-, is much more likely to be found attached to H^+, as HA, than as unattached A^-. That is, the equilibrium

$$H_2O(l) + A^-(aq) \rightleftharpoons HA(aq) + OH^-(aq)$$

rests heavily on the side of products. A consequence of this attachment process is an increase in the concentration of OH^- and so a decrease in the concentration of H_3O^+ (since their concentrations are inversely related through the water autoionization equilibrium). The result is that *solutions of salts of weak acids are basic*.

In an analogous way we can see that *solutions of salts of weak bases are acidic*. The conjugate acid, BH^+, of the weak base, is more likely to exist as the unattached base, B. That is, the equilibrium

$$BH^+(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + B(aq)$$

strongly favors products. This donation of the proton to the water makes the solution acidic.

The reaction of the conjugate base (acid) of a weak acid (base) with water is called *hydrolysis*, because the effect is to break apart water. We can calculate the pH due to the hydrolysis by solving the hydrolysis equilibrium expression. The equilibrium constant is related to the equilibrium constant of the weak acid (base) as

$$K_b = K_w / K_a \ (K_a = K_w / K_b).$$

For example, let's calculate the pH of 1.000 M ammonium chloride, formed by neutralization of ammonia (a weak base) by hydrochloric acid (a strong acid). The K_b of ammonia is 1.8×10^{-5}, and so the K_a of the conjugate acid NH_4^+ is 5.6×10^{-10}.

Note that because K_w is so small, usually the hydrolysis equilibrium constant is quite small. Here is the table of initial and equilibrium concentrations.

	$[NH_4^+]/M$	$[H_3O^+]/M$	$[NH_3]/M$
initial	1.	$1. \times 10^{-7}$	0.
equilibrium	$1. - 1.\,x$	$1. \times 10^{-7} + x$	x

Initial and equilibrium activities for the hydrolysis of 1.000 M NH_4^+.

Now, we can approximate x as large compared to 10^{-7}, since the resulting solution will be acidic, and we can approximate x as small compared to 1.000, since the equilibrium constant is so small. This leads to

$$K_a = \frac{(x + 10^{-7})\,x}{c_a - x} \approx \frac{x^2}{c_a}$$

and so

$$x \approx \sqrt{c_a K_a}$$

This evaluates to $x = 2.4 \times 10^{-5}$.

> Calculate the pH of 1.000 M ammonium chloride at 25°C.

In a similar way you can calculate that solutions of the salt of a weak acid will be basic.

> Calculate the pH of a 1.000 M solution of sodium acetate at 25°C. Note that sodium acetate when dissolved in water dissociates into sodium ions and acetate ions, and that acetate is the conjugate base of the weak acid acetic acid.

> Explain quantitatively why we do not need to worry about hydrolysis of the salts of strong acid neutralized by a strong base.

■ When hydrolysis is important: Weak can be strong!

We have learned that aqueous solutions of salts of weak acids are *basic*, and that aqueous solutions of salts of weak bases are *acidic*. The reason these solutions have pH different from that of pure water is because the salts *hydrolyze water*. The hydrolysis equations are

$$H_2O(l) + A^-(aq) \rightleftharpoons HA(aq) + OH^-(aq),\ \ \text{pH} > 7\ (\text{basic})$$

$$BH^+(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + B(aq).\ \text{pH} < 7\ (\text{acidic})$$

The question is, *why do such salts hydrolyze water?*. The answer, as we have seen, is because HA is preferred over A^-, since HA is a weak acid, and because B is preferred over BH^+, since B is a weak base; therefore the equilibrium point of the hydrolysis equations is far to the product (HA and B) side.

Now, here is another way to look at these results. Let's consider three different acids, HCl ($K_a = 10^7$), H_2O (viewed as an acid), and a weak acid HA with $K_a = 10^{-5}$. The hydrolysis reactions and equilibrium constants of the corresponding conjugate bases are

$$H_2O(l) + Cl^-(aq) \rightleftharpoons HCl(aq) + OH^-(aq),\ \ K_b = K_w / 10^7 = 10^{-21},$$

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq),\ \ K_b = K_w = 10^{-14},$$

$$H_2O(l) + A^-(aq) \rightleftharpoons HA(aq) + OH^-(aq),\ \ K_b = K_w\, 10^{-5} = 10^{-9}.$$

The first thing to notice is that each of the conjugate bases is quite weak in the absolute sense, that is, in each case $K_b \ll 1$. The second thing to notice, however, in that in a relative sense, the conjugate base of the strong acid is a weaker base than water, $K_b(\text{HCl}) \ll K_w$, and so a lesser source of OH^-, while the conjugate base of the weak acid is a stronger base than water, $K_b(A^-) \gg K_w$and so a greater source of OH^-.

This analysis shows that we can ignore hydrolysis by the conjugate base of a strong acid, in the sense that this hydrolysis has negligible effect on OH^- concentration compared to the autoionization of water. On the other hand, we cannot ignore hydrolysis by the conjugate base of a weak acid, in the sense that this hydrolysis results in OH^- concentration that dwarfs that due to the autoionization of water.

> Construct the analogous comparison to water of the strength of hydrolysis of the conjugate acids of the strong base NaOH and a weak base B, with $K_b = K_w / 10^{-5}$.

Sometimes hydrolysis is explained by saying that the conjugate base, A^-, of a weak acid is a *strong base*. What is meant is strong relative to water, since A^- has greater affinity for H^+ than does H_2O. Similarly the conjugate acid, BH^+, of a weak base is said to be a *strong acid*; what is meant is that BH^+ has less affinity for H^+ than does H_2O. As our analysis shows, however, the conjugate base of a weak acid is *not* strong in an absolute sense, that is, its K_b is not large compared to 1; however, its K_b *is* large compared to K_w. Similarly, the conjugate acid of a weak base is *not* strong in the sense that its K_a is not large compared to 1; but its K_a *is* large compared to K_w.

The key idea is that in hydrolysis, it is the acid or base strength *relative to water*, not the absolute strength, that matters. Only in this sense do weak acids have strong conjugate bases, and do weak bases have strong conjugate acids.

The shift in perspective from absolute to relative acid or base strength is important in other contexts too, for example, in organic chemistry where processes occur in solvents in which no water at all is present. But that is for another course.

Regime 2: Partially neutralized weak acid (or base): buffer

If we add base to a weak acid, but the moles of base added are not sufficient to consume all of the acid originally present, then after the acid and base have reacted, some unreacted acid will remain. The acid that has been consumed by the added base will have been converted into the conjugate base of the acid. This means that after the reaction between the acid originally present and the base that is added there will be present *unreacted weak acid and conjugate base of the weak acid*.

Such a solution of a weak acid and its salt is known as a *buffer* because it has the almost magical property that if you add a strong acid or base to it, the *pH changes hardly at all!* We say the solution *buffers* the effect of added acid or base.

To see how this works, let's say we have a weak acid buffer, say a solution of acetic acid (HA) and sodium acetate (which comes apart in solution into Na^+ and A^-). If a strong acid is added, the hydronium ions are consumed by attachment to the conjugate base,

$$H_3O^+(aq) + A^-(aq) \rightleftharpoons HA(aq) + H_2O(l).$$

Because HA is a weak acid, this equilibrium heavily favors products, as we have seen in our treatment of hydrolysis.

If instead a strong base is added, the OH^- reacts with the weak acid,

$$HA(aq) + OH^-(aq) \rightleftarrows H_2O(l) + A^-(aq).$$

Because water is a much weaker acid than HA (or, equivalently, because OH^- is a much stronger base—H^+ acceptor—than A^-), this equilibrium heavily favors products. The net result is that both added H_3O^+ and OH^- are consumed by reaction with the buffer, and so the pH changes only by a small amount.

■ Calculation of buffer action

We can see quantitatively how buffers work, by computing the pH of an acetic acid-sodium acetate solution. The acid ionization constant of acetic acid is 1.76×10^{-5}. The sodium acetate dissociates essentially completely to give acetate ions, the conjugate base of acetic acid. Let's take the total volume of the solution to be 1.000 L and the *label concentration* (that is, *not* taking into account any equilibration) of the acetic acid to be $c_a = 1.000$ M, and of its conjugate base to be $c_b = 1.000$ M.

Here is the table of initial and equilibrium concentrations of the acid ionization equilibrium.

	$[HA]/M$	$[H_3O^+]/M$	$[A^-]/M$
initial	c_a	$1. \times 10^{-7}$	c_b
equilibrium	$-x + c_a$	$1. \times 10^{-7} + x$	$x + c_b$

Initial and equilibrium activities for buffer composed of 1.000 M acetic acid and 1.000 M sodium acetate.

The chemical equation is

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

and so the equilibrium expression is

$$K_a = \frac{(10^{-7} + x)(c_b + x)}{c_a - x}.$$

As usual, we will approximate x as large compared to 10^{-7}. Since HA is a here a weak acid, it contributes only a small additional amount of conjugate base (acetate ions in this case), and this means x is negligible compared to c_a and c_b. The equilibrium expression then becomes

$$K_a \approx \frac{x\, c_b}{c_a}$$

and so the equilibrium hydronium concentration is given by

$$x \approx K_a\, c_a / c_b.$$

This evaluates to $x = 1.76 \times 10^{-5}$. This is indeed small comparted with c_a and c_b, and is indeed large compare with 10^{-7}, so our approximations are justified.

> Calculate the pH of this buffer solution. Answer: 4.754.

> Calculate the pH for $c_a = 0.900$ M and $c_b = 1.100$ M. Answer: 4.842.

■ Adding strong acid to a weak-acid buffer

Now, let's add 100 mL of 1.000 M HCl to the buffer solution. What will be the pH of the resulting solution? To answer this question we must proceed in two steps.

1. *Limiting-reagent stoichiometry*: First, let what is added (HCl) react 100%, as a *limiting reagent problem*, with what it is added to. This will change the concentrations of HA and A^-. We need to do this calculation *in moles* (a limiting reagent problem), and then use the total volume to convert the resulting moles into concentrations (molarities).

2. *Re-equilibration*: Second, use the changed concentrations of HA and A^- to compute the new equilibrium.

Step 1: Limiting-reagent stoichiometry

We have added 0.100 L × 1.000 M = 0.100 mol HCl. This reacts with the A^- to form HA as

$$\mathrm{HCl}(aq) + \mathrm{A}^-\,(aq) \rightarrow \mathrm{HA}(aq) + \mathrm{Cl}^-\,(aq).$$

	mol HCl	mol A^-	mol HA
initial	0.1	1	1
final	0	0.9	1.1

Initial and final moles for reaction of HCl with a mixture of acetic acid and sodium acetate.

Note that the limitng reagent reaction is *not* written as an equilibrium, since we assume 100% reaction at this stage. This assumption makes sense because HA is a much weaker acid than HCl, or, equivalently, A^- is a much stronger base (proton acceptor) than Cl^-. In this step we ignore the HA–A^- equilibrium. We can do this because we will take into account the equilibration of the HA and A^- in the second step.

> Show that the result is that the concentration of HA and A^- are now $c_a = 1.000$ M and $c_b = 0.818$ M.

Note that we have taken into account the changed volume resulting from the addition of the HCl solution. It is essential to always do this.

Step 2: Re-equilibration

The concentrations we have computed as a result of the limiting reagent analysis are *initial* concentrations as far as the HA-A equilibrium is concerned, since in the limiting-reagent reaction we have ignored the weak acid dissociation equilibrium. We can recalculate the equilibrium concentration of H_3O^+ with these new concentrations.

> Show that the result is $x = 2.15 \times 10^{-5}$ and that the corresponding pH is 4.667.

Compare this to what the pH would be if we added 100 mL of 0.100 M HCl to 1.000 L of pure water. The H_3O^+ concentration then would be just the moles of HCl added (since HCl dissociates nearly 100%) divided by the total volume.

> Show that this H_3O^+ concentration is 0.00909 M, and so that the pH would be 2.041.

Adding 100 mL of 0.100 M HCl to the 1.000 L of buffer changes the pH from 4.754 to 4.667, whereas dding 100 mL of 0.100 M HCl to 1.000 L of pure water changes the pH from 7 to 2.041.

■ Adding strong base to a weak-acid buffer

Now, let's add 100 mL of 1.000 M NaOH to the buffer solution. What will be the pH of the resulting solution? As before we must proceed in two steps.

Step 1: Limiting-reagent stoichiometry

We have added 0.100 L × 1.000 M = 0.100 mol NaOH. This reacts with the HA to form A^- as

$$HA(aq) + NaOH(aq) \rightarrow H_2O(l) + A^-(aq) + Na^+(aq)$$

	mol HA	mol NaOH	mol A^-	mol Na^+
initial	1	0.1	1	0
final	0.9	0	1.1	0.1

Initial and final moles for reaction of NaOH with a mixture of acetic acid and sodium acetate.

Again, this is *not* written as an equilibrium, since we assume 100% reaction.

> Show that the result is that the concentrations of HA and A^- are now $c_a = 0.818$ M and $c_b = 1.000$ M.

Step 2: Re-equilibration

We can recalculate the equilibrium concentration of H_3O^+ with these new concentrations.

> Show that the result is $x = 1.44 \times 10^{-5}$ and so that the pH is 4.842.

Compare this to what the pH would be if we added 100 mL of 0.100 M NaOH to 1.000 L of pure water. The OH^- concentration would be just the moles of NaOH added (since NaOH dissociates 100 %) divided by the total volume.

> Show that the hydroxide ion concentration would be 0.0909 M, and so that the pOH and pH would be 1.041 and 12.959.

The buffer pH has changed from 4.754 to 4.842, whereas in the absence of the buffer the pH change would be from 7 to 12.959.

■ Comparison to unbuffered solution

Here is a summary of results compared with pure water.

	pure solution	add strong acid	add strong base
pure water	7	1.041	12.959
weak-acid buffer	4.754	4.667	4.842

Effect on pH of added base to 1 L of pure water and to 1 L of a 1.000 M/1.000 M acetic acid/sodium acetate buffer at 25°C.

We see that the buffer nearly completely eliminates the effect of added acid and base.

■ Henderson-Hasselbalch equation

We have seen that the equilibrium expression for a weak-acid buffer is

$$K_a = \frac{(10^{-7} + x)\,(c_b + x)}{c_a - x}$$

We have also seen that we can approximate this expression in two ways.

1. When $K_a \gg K_w$, then the H_3O^+ from the water autoionization (10^{-7}) is negligible compared to that from the acid ionization (x). This means that $10^{-7} + x$ is approximately just x.
2. When $K_a \ll 1$ (as it is for a weak acid), then the amount of acid that ionizes (x) is small compared to the acid and conjugate base originally present (c_a and c_b). This means that $c_a - x$ is approximately c_a and $c_b + x$ is approximately c_b.

With these approximations, the equilibrium expression becomes

$$K_a = \frac{x\,c_b}{c_a}$$

where x is the (numerical value of) the equilibrium molarity of H_3O^+. Solving for $[H_3O^+]$, we get

$$\frac{[H_3O^+]}{M} = x = \mathrm{K}_a\,\frac{c_b}{c_a}.$$

Now, we can use this relation to get an expression for pH, by taking the negative logarithm (base 10) of both sides,

$$-\log_{10}([H_3O^+]/\mathrm{M}) = -\log_{10}\left(\mathrm{K}_a\,\frac{c_b}{c_a}\right) = -\log_{10}(K_a) + \log_{10}\left(\frac{c_b}{c_a}\right).$$

We can rewrite this result compactly as

$$\mathrm{pH} = \mathrm{pK}_a + \log_{10}\left(\frac{c_b}{c_a}\right).$$

This is known as the *Henderson-Hasselbalch equation*, for the pH of a weak-acid buffer.

> Under what conditions will the pH computed from the *Henderson-Hasselbalch equation* be correct? Answer: $1 \gg K_a \gg K_w$.

I do not ever use this formula myself, since I always develop the formulas I need as part of the solution to each problem. However, if you are doing many different calculations with buffers, and the necessary conditions hold, then the Henderson-Hasselbalch equation is very useful.

Regime 4: Excess base (or acid)

If we add base to a weak acid, and the moles of base added are in excess of the acid originally present, then after the acid and base have reacted, all of the acid will have been consumed and some unreacted base will remain. This means that after the reaction between the acid originally present and the base that is added there will be present *unreacted strong base and the conjugate base of the weak acid*. For example, say we add 1.2 L of 1.000 M sodium hydroxide to 1.0 L of 1.000 M acetic acid.

$$\mathrm{HA}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{H_2\,O}(l) + \mathrm{A^-}\,(aq) + \mathrm{Na^+}\,(aq)$$

	mol HA	mol NaOH	mol A^-	mol Na^+
initial	1	1.2	0	0
final	0	0.2	1	1

Initial and final activities for reaction of NaOWith a mixture of acetic acid and sodium acetate.

After the reaction what remains is two bases: the unreacted added base, sodium hydroxide, and the conjugate base, acetate, formed in the reaction with the acid. Because the sodium hydroxide is 100% dissociated, its contribution to the OH^- concentration is equal to the number of moles of sodium hydroxide, divided by the total volume.

> Show that the OH^- concentration is 0.09 M.

Because acetate is a weak base, its contribution to the OH^- concentration, through the hydrolysis

$$H_2O(l) + A^-(aq) \rightleftharpoons HA(aq) + OH^-(aq),$$

is much smaller and so can be neglected.

> Show that the contribution to the OH^- concentration due to hydrolysis (in pure water) by the acetate is 1.61×10^{-5} mol/L, and so indeed negligible compared to the contribution to the OH^- concentration due to the unreacted sodium hydroxide.

The net result is that when excess strong base is present, there is no need to solve an equilibrium. Rather, the OH^- is just the moles of unreacted strong base divided by the total volume.

Practice with regimes

The key to finding our way in acid-base equilibrium problems is to know what regime applies. This is because once we know the regime, we know which equilibrium expressions to use. For each of the following circumstances, determine which of the four regimes applies and then evaluate the pH. Assume 1 L of each solution are combined.

> 1 M ammonia and 0.5 M HCl. Answer: 9.25.

> 1 M sodium acetate and 1 M acetic acid. Answer: 4.76.

> 1 M sodium acetate and 1 M HCl. Answer: 2.53.

> 1 M HCl and 1 M acetic acid. Answer 0.301.

> 1 M HCl , 1 M acetic acid, and 1 M sodium acetate. Answer: 2.47.

> 1 M sodium hydroxide and 1 M sodium acetate. Answer: 13.70.

> 1 M HCl and 0.5 M ammonia. Answer: 0.602.

> 1 M HCl and 1 M ammonia. Answer: 4.78.

The way to solve these problems is to, as a first step, let any acids and bases react together 100 % as a limiting reagent problem. It is crucial to do this step *completely ignoring all weak acid and weak* *base equilibria* (including hydrolysis). The reason to ignore these equilibria is that, they can be properly treated *only as a second step*, that is, only once we know which regime we are dealing with.

As example, consider a mixture of NaOH and ammonium chloride. Since ammonium, NH_4^+ (from the dissociation of the ammonium chloride) is a weak acid, we need to consider as a first step the limiting reagent reaction

$$NH_4^+\,(aq) + NaOH(aq) \rightleftarrows H_2\,O(l) + NH_3\,(aq) + Na^+\,(aq)$$

There are three possibilities. If there are more moles of NH_4^+ than of NaOH, then after the reaction we have a combination of unreacted NH_4^+ and some NH_3, that is, a weak base and its conjugate acid (regime 2). If there are equal moles of NH_4^+ and of NaOH, then after the reaction all of the NH_4^+ and NaOH are consumed and we have just pure weak base, NH_3 (regime 1). Finally, if there are more moles of NaOH than of NH_4^+, then not all of the NaOH is consumed and so we have an excess strong base problem (regime 4).

Putting it all together: titration

In titration of acids and bases we measure the change in pH as we add base (or acid) of a known concentration to a given volume of an acid (or base) of known concentration. Neutralization occurs at the *equivalence point*, when the moles of base (or acid) added exactly equals the moles of acid (or base) originally present. There are four regimes that need to be treated differently:

1. The pH of the original acid (or base).
2. The pH when the acid (or base) has been only partial neutralized.
3. The pH at the equivalence point.
4. The pH when excess base (or acid) has been added, that is, after the equivalence point.

In computing the pH for different points in regimes 2, 3 and 4 it is important to always carry out the limiting reagent part of the analysis starting with the *original* amounts present, rather than the amounts determined at the previous titration point. There are two reasons to do this. First, the limiting reagent step can be done all at once rather than having to adjust its results by taking into account concentrations from a previous step. Second, in this way we avoid accumulation of small errors due to approximations made in calculating the concentrations at previous steps.

■ Strong acid/strong base titration

Here is how to calculate pH in the different regimes of titration of a strong acid with a strong base. Let's titrate 100.0 mL of 0.100 M HCl with 0.120 M NaOH. The equivalence point is when

$$\text{moles of acid} = M_a\,V_a = \text{moles of base} = M_b\,V_b$$

The *equivalence volume*, the volume of base needed to just react with all of the acid originally present is therefore given by

$$V_{\text{equivalence}} = V_a\,\frac{M_a}{M_b}.$$

> Show that for our case this evaluates to 83.3 mL

When this volume of base has been added, the acid will have been exactly neutralized. If less than this volume of base is added, the solution will contain unreacted acid. If more than this volume of base is added the solution will contain excess base.

Regime 1: pH of pure acid

Because HCl is a strong acid, it is essentially 100% dissociated, and so its pH is just the negative logarithm of (the numerical value of) its molarity, pH == −log(0.100) = 1.000.

Regime 2: pH of partially neutralized acid

Since the equivalence point occurs when 83.3 mL of base is added, if only 40.0 mL (say) of base is added, then the acid will only be partially neutralized. We need to treat the partial neutralization as a limiting reagent problem, *using moles* (not molarity).

	mol HCl	mol NaOH	mol Cl^-	mol Na^+
initial	0.01	0.0048	0	0
final	0.0052	0	0.0048	0.0048

Initial and final moles for reaction of 40.00 mL of 0.120 M NaOH with 100.0 mL of 0.100 M HCl.

> Verify that the values given in this table are correct.

> What would the values be if instead 50 mL of 0.120 M NaOH had been added?

Since we have added less than the equivalence volume of base, unreacted acid remains.

> Show that the concentration of the unreacted acid is now 0.037 M.

This molarity is less than the original acid molarity because the volume of the solution has increased. Once we know the molarity of the unreacted acid we can compute the new pH.

> Show that the new pH is 1.430.

Regime 3: pH of exactly neutralized acid

When 83.3 mL of NaOH is added, the HCl will have been completely converted to water and NaCl. Since neither Na^+ nor Cl^- hydrolyzes water (because NaOH is a strong base and HCl is a strong acid), the pH at the equivalence point is 7.

Regime 4: pH of excess base

What will the pH be if we add more that the equivalence volume of base, say 100.0 mL? We are adding 0.1000 L × 0.120 M = 0.0120 moles of NaOH. Again, we need to treat the reaction of the base and acid as a limiting reagent problem, using moles (not molarity).

	mol HCl	mol NaOH	mol Cl^-	mol Na^+
initial	0.01	0.012	0	0
final	0	0.002	0.01	0.01

Initial and final moles for reaction of 100.00 mL of 0.120 M NaOH with 100.0 mL of 0.100 M HCl.

Now the acid is the limiting reagent; not all of the base has reacted; some is left over.

> Show that the concentration of the unreacted base is 0.010 M.

To determine the pH, we first compute the pOH of the excess base, using its molarity since it is 100% dissociated, and then use this to calculate the pH.

> Show in this way that the pH is 12.000.

Calculation of titration curve

Here is a *Mathematica* function to calculate the pH during the titration of volume V_a of a strong acid of molarity M_a by a strong base of molarity M_b.

```
pHstrong[Ma_, Va_, Mb_, Vb_] := Block[{
   Kw = 10^-14,
   Vequiv = Va Ma/Mb
  },
  -Log[10, Which[
     Vb / L == 0 (* pure weak acid *), Ma/(mol / L),
     Vb / L < Vequiv / L(* buffer *), ((Va Ma - Vb Mb)/(Va + Vb)) L/mol,
     Vb / L == Vequiv / L (* hydrolysis *), √Kw ,
     Vb / L > Vequiv / L (* excess base *), Kw (Va + Vb)/(Vb Mb - Va Ma) mol/L
    ]
   ]
  ]
```

This function calculates the pH using $[H_3O^+]$ calculated appropriately depending on whether the added base volume corresponds to regime 1 ($V_b = 0$), 2 ($0 < V_b < V_{\text{equiv}}$), 3 ($V_b = V_{\text{equiv}}$) or 4 ($V_b > V_{\text{equiv}}$). The expression for $[H_3O^+]$ for regime 4, $V_b > V_{\text{equiv}}$, is written compactly using

$$\text{pH} = 14 - \text{pOH} = -\log_{10}(K_w) + \log_{10}\left(\frac{[\text{OH}^-]}{\text{mol}/\text{L}}\right) = -\log_{10}\left(\frac{K_w\,\text{mol}/L}{[\text{OH}^-]}\right).$$

> The *Mathematica* function calculates the H_3O^+ activity (numerical value of its molarity) beyond the equivalence point, $V_b = V_{\text{equiv}}$, using the formula
>
> $$K_w(\text{mol}/L)\,(V_a + V_b)/(V_b\,M_b - V_a\,M_a).$$
>
> Derive this formula.

Here are the values K_a, M_a, V_a and V_b,

```
Ma = 0.100 mol / L;
Va = 0.100 L;
Mb = 0.120 mol / L;
```

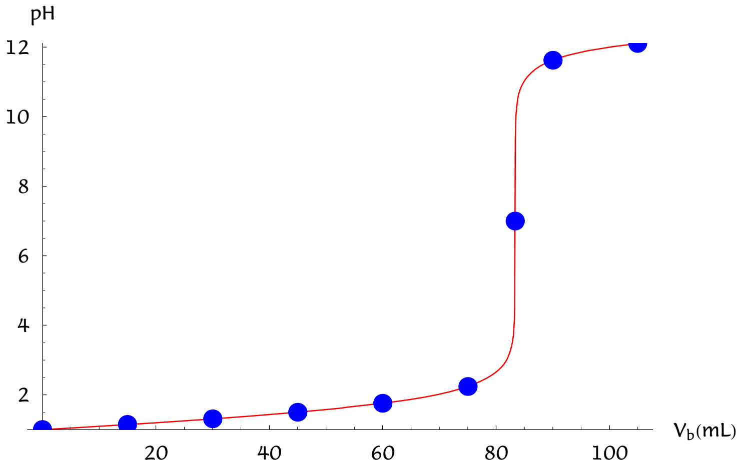
> Show that the equivalence volume is 83.3 mL.

Here are the corresponding pH values for the various volumes of base added.

```
    mL        pH
   0.000     1.000
  15.000     1.147
  30.000     1.308
  45.000     1.499
  60.000     1.757
  75.000     2.243
  83.333     7.000
  90.000    11.624
 105.000    12.103
```

pH of 100.0 mL of 0.100 M HCl ($K_a = 1 \times 10^7$) versus mL of added 0.120 M NaOH.

Here is a graph of pH versus the total volume of base added.



Titration of 100.0 mL of 0.100 M HCl ($K_a = 1 \times 10^7$) with 0.120 M NaOH. pH is plotted versus mL of base added.

The points mark the pH values for the specific volumes.

■ Weak acid/strong base titration

Here is how to calculate pH in the different regimes of titration of a weak acid with a strong base. Titrate 100.0 mL of 0.100 M acetic acid ($K_a = 1.76 \times 10^{-5}$) with 0.120 M NaOH. Do this by calculating the pH for 0, 15.0, 45.0, 60.0, 75.0, 90.0, 105 and 120 mL of NaOH added. Also calculate the equivalence volume and the pH at the equivalence point. If you can, plot your results as pH versus mL of base added.

Here are some hints for solving this problem.

- For no volume added, we have a pure weak acid problem.
- For volumes of base less than the equivalence volume, we have to do buffer calculations.
- At the equivalence point, we have a hydrolysis problem.
- For volumes beyond the equivalence point, we have just a strong base problem.

Let's summarize how to treat each of these cases.

Equivalence volume

The *equivalence volume* is the volume of base that contains the same number of moles of base as there are moles of acid originally present. Since

$$\text{mol acid} = V_a M_a = \text{mol base} = V_{\text{equiv}} M_b$$

the equivalence volume is given by

$$V_{\text{equiv}} = V_a \frac{M_a}{M_b}$$

Pure weak acid

The equilibrium expression for a pure weak acid of concentration M_a is

$$K_a = \frac{x^2}{M_a},$$

$$x = \frac{[\mathrm{H_3O^+}]}{\mathrm{mol/L}} = \sqrt{M_a K_a}\,.$$

Here we have approximated x as large compared with 10^{-7} and small compared with M_a.

Partial neutralization of weak acid by strong base

If volume V_b of a strong base of concentration M_b is added to volume V_a of a weak acid of concentration M_a, $V_b\,M_b$ moles of base will react with the acid. The result will be the conversion of $V_b\,M_b$ moles of acid into and equal number of moles of conjugate base, and $V_a\,M_a - V_b\,M_b$ moles of acid will remain, Therefore, the concentration of the acid is reduced from M_a to

$$c_a = \frac{V_a\,M_a - V_b\,M_b}{V_a + V_b}$$

and the concentration of conjugate base—originally zero—is now

$$c_b = \frac{V_b\,M_b}{V_a + V_b}$$

These are the starting concentrations that we use to determine the final equilibrium between the weak acid and its conjugate base, using the equilibrium expression.

$$K_a = x\,\frac{c_b}{c_a},$$

$$x = \frac{[\mathrm{H_3O^+}]}{\mathrm{mol/L}} = K_a\,\frac{c_a}{c_b} = K_a\,\frac{V_a\,M_a - V_b\,M_b}{V_a\,M_b}.$$

Here we have approximated x as large compared with 10^{-7} and small compared with both c_a and c_b. Notice that in the ratio of concentrations, c_a / c_b, the total volume divides out.

Exact neutralization of weak acid by strong base

When there is exact neutralization, then all of the strong base is exactly consumed and all of the weak acid is converted to its conjugate base. The concentration of the conjugate base produced is

$$c_b = \frac{V_a\,M_a}{V_a + V_b}.$$

The equilibrium concentration x of $\mathrm{OH^-}$ satisfies

$$K_b = \frac{K_w}{K_a} = \frac{x^2}{c_b},$$

$$x = \frac{[\mathrm{OH}^-]}{\mathrm{mol/L}} = \sqrt{c_b\,K_b} = \sqrt{c_b\,K_w/K_a}\,.$$

Here we have approximated x as large compared with 10^{-7} and small compared with c_b.

Excess strong base

When excess base is added, then all of the acid is converted to $V_a\,M_a$ moles of conjugate base, and $V_b\,M_b - V_a\,M_a$ moles of base remain. We can ignore the OH^- produced by hydrolysis of the conjugate base, since it is much smaller that the OH^- due to the excess base; the concentration OH^- is just the concentration of the excess base is

$$[\mathrm{OH}^-] = \frac{V_b\,M_b - V_a\,M_a}{V_a + V_b}$$

We ignore the contribution to the OH^- concentration due to the hydrolysis of water by the conjugate base of the weak acid.

> Why is this justified?

Calculation of pH

Here is a *Mathematica* function to calculate the pH during the titration of volume V_a of a weak acid of molarity M_a and ionization constant K_a by a strong base of molarity M_b.

```
pHweak[Ka_, Ma_, Va_, Mb_, Vb_] := Block[{
   Kw = 10^-14,
   Vequiv = Va Ma/Mb
  },
  -Log[10, Which[
    Vb / L == 0 (* pure weak acid *), Sqrt[Ma/(mol / L) Ka],
    Vb / L < Vequiv / L(* buffer *), Ka (Va Ma - Vb Mb)/(Vb Mb),
    Vb / L == Vequiv / L (* hydrolysis *), Sqrt[Ka Kw (Va + Vb)/(Va Ma) mol/L],
    Vb / L > Vequiv / L (* excess base *), Kw (Va + Vb)/(Vb Mb - Va Ma) mol/L
   ]
  ]
 ]
```

This function calculates the pH using $[\mathrm{H_3O^+}]$ calculated appropriately depending on whether the added base volume corresponds to regime 1 ($V_b = 0$), 2 ($0 < V_b < V_{\mathrm{equiv}}$), 3 ($V_b = V_{\mathrm{equiv}}$) or 4 ($V_b > V_{\mathrm{equiv}}$). The expressions for $[\mathrm{H_3O^+}]$ for regime 3, $V = V_{\mathrm{equiv}}$, and regime 4, $V_b > V_{\mathrm{equiv}}$, are written compactly using

$$\mathrm{pH} = 14 - \mathrm{pOH} = -\log_{10}(K_w) + \log_{10}\left(\frac{[\mathrm{OH}^-]}{\mathrm{mol/L}}\right) = -\log_{10}\left(\frac{K_w\,\mathrm{mol}/L}{[\mathrm{OH}^-]}\right).$$

> The *Mathematica* function calculates the H_3O^+ activity (numerical value of its molality) at the equivalence point, $V_b = V_{\text{equiv}}$, using the formula
>
> $$\sqrt{K_a\,K_w(\text{mol}/L)\,(V_a+V_b)/(V_a\,M_a)}\,.$$
>
> Derive this formula.

Results

Here are the values K_a, M_a, V_a and V_b for the study problem.

```
Ka = 1.76 × 10^-5;
Ma = 0.100 mol / L;
Va = 0.100 L;
Mb = 0.120 mol / L;
```

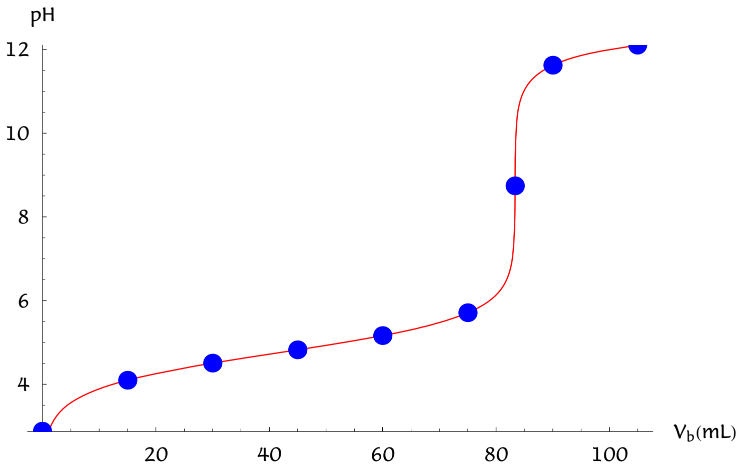
> Show that the equivalence volume is 83.3 mL.

Here are the corresponding pH values for the various volumes of base added.

```
   mL        pH
  0.000     2.877
 15.000     4.096
 30.000     4.505
 45.000     4.824
 60.000     5.165
 75.000     5.709
 83.333     8.746
 90.000    11.624
105.000    12.103
```

pH of 100.0 mL of 0.100 M acetic acid ($K_a = 1.76 \times 10^{-5}$) versus mL of added 0.120 M NaOH.

Here is a graph of pH versus the total volume of base added.

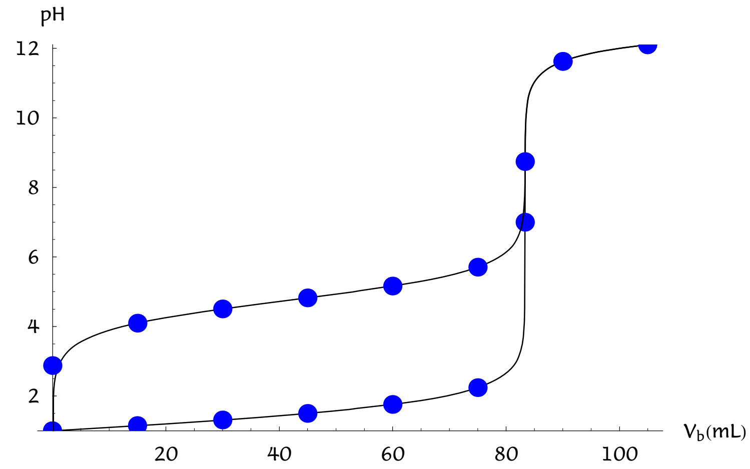


Titration of 100.0 mL of 0.100 M acetic acid ($K_a = 1.76 \times 10^{-5}$) with 0.120 M NaOH. pH is plotted versus mL of base added.

The points are mark the pH values for the specific volumes.

■ Strong acid–strong base versus weak acid–strong base titration

Here is a comparison of the titration curves for 100.0 mL of 0.100 M HCl and for 100.0 mL of 0.100 M acetic acid with 0.120 M NaOH.



Titration of 100.0 mL of 0.100 M acetic acid ($K_a = 1.76 \times 10^{-5}$, upper curve) and titration of 100.0 mL of 0.100 M HCl ($K_a = 1 \times 10^{7}$, lower curve) with 0.120 M NaOH. pH is plotted versus mL of base added.

> How do the two curves compare for small amounts of added base?

> How do the two curves compare for amounts of added base near one-half the equivalence volume?

> Why are the two curves the same for amounts of added base greater than the equivalence volume?

> What is the total pH change as the total volume of base added changes from 15 mL to 75 mL for each of the curves? Based on your result, which curve is more effective at maintaining pH within a narrow range? Are you surprised by your result?

> Is there a circumstance in which a strong acid could act as a good buffer?

> Sketch on the plot the weak acid curve for K_a increased by a factor of $10^{1.5}$ and K_a decreased by the same factor.

■ Limiting-reagent calculations in titrations: Study problems

We have seen that the calculation of strong-acid/strong-base titration involves only the stoichiometry of the acid-base reaction. Titrations involving weak acids or weak bases involve, as we have seen, in addition the calculation of the re-equilibration using the new concentrations resulting from the limiting-reagent stoichiometry calculations. Here are two problems that illustrate the crucial importance of first letting what is added react with what is already present as a limiting-reagent problem.

Add strong base to a weak acid to give a particular pH

The problem is to determine the volume x of M_b = 0.0500 M NaOH to add to V_a = 500 mL of M_a = 0.100 M formic acid ($K_a = 1.77 \times 10^{-4}$) to make the pH of the combined solution 3.00. The limiting-reagent reaction in this case is the reaction of the OH^- (from the NaOH) with the formic acid (which we write as HA), to give the conjugate base (A^-) of the formic acid,

$$HA(aq) + OH^-(aq) \rightarrow H_2O(l) + A^-(aq).$$

Because this reaction is assumed to proceed 100%, we do *not* use a double arrow. The number of moles of A^- formed in this way is $x\,M_b$, the number of moles of weak acid remaining is $V_a\,M_a - x\,M_b$, and so the concentrations are

$$c_a = \frac{V_a\,M_a - x\,M_b}{V_a + x},$$

$$c_b = \frac{x\,M_b}{V_a + x}.$$

We use these concentration to do the second step of the problem, namely to determine the equilibrium

$$\mathrm{HA}(aq) + \mathrm{H_2\,O}(l) \rightleftarrows \mathrm{H_3\,O^+}\,(aq) + \mathrm{A^-}\,(aq)$$

$$K_a = [\mathrm{H_3O^+}]\,\frac{\mathrm{c}_b}{c_a}$$

where we approximate the additional ionization y of the acid as small compared to c_a and c_b. We do *not* need to make any approximate to $[\mathrm{H_3O^+}] = 10^{-7} + y$, because we know from the pH that $[\mathrm{H_3O^+}] = 10^{-3.00}$. The equilibrium relation becomes

$$K_a = 10^{-\mathrm{pH}}\,\frac{x\,M_b}{V_a\,M_a - x\,M_b}$$

which we can solve for the unknown volume x.

> Show that $x = 150$ mL.

Add strong acid to a weak-acid salt to give a particular pH

In this problem we need to find the volume x of $M_a = 0.100$ M HCl to add to $V_b = 400$ mL of $M_b = 0.0800$ M NaCN, so that the pH of the combined solution is 9.58. The limiting-reagent reaction here is

$$\mathrm{HCl}(aq) + \mathrm{CN^-}\,(aq) \to \mathrm{HCN}(aq) + \mathrm{Cl^-}\,(aq)$$

and with itwe can determine the initial molarity c_a of the HCN ($K_a = 4.93 \times 10^{-10}$) and c_b of the $\mathrm{CN^-}$, in terms of the unknown volume x

$$c_b = \frac{V_b\,M_b - x\,M_a}{V_b + V_a},$$

$$c_a = \frac{x\,M_a}{V_b + V_a}.$$

Then we can set up the equilibrium

$$\mathrm{HCN}(aq) + \mathrm{H_2\,O}(l) \rightleftarrows \mathrm{H_3\,O^+}\,(aq) + \mathrm{CN^-}\,(aq),$$

use $[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} = 10^{-9.58}$ and then solve its equilibrium expression for the volume x. The expression is

$$K_a = 10^{-\mathrm{pH}} \frac{V_b M_b - x M_a}{x M_a}.$$

> Show that $x = 111$ mL.

■ Titration recipes

I have collected into a document the various results needed to calculate aqueous acid-base titrations. It is on the Web at

http://quantum.bu.edu/notes/GeneralChemistry/titration-recipes.pdf

I hope the recipes are helpful.

Polyprotic acids

Acids such as H_2SO_4 and H_2CO_3 are called *polyprotic acids*, because they are able to donate more than one proton in successive ionization equilibria. For example, carbonic acid ionization proceeds as

$$\mathrm{H_2\,CO_3}(aq) + \mathrm{H_2\,O}(l) \rightleftarrows \mathrm{H_3O^+} + \mathrm{HCO_3^-}(aq),\ \ K_{\mathrm{a1}},$$

and

$$\mathrm{HCO_3^-}\,(aq) + \mathrm{H_2\,O}(l) \rightleftarrows \mathrm{H_3O^+} + \mathrm{CO_3^{2-}}\,(aq),\ \ K_{\mathrm{a2}}.$$

Generally, exact calculation of the equilibrium concentration of the acid, and its successively produced conjugate bases is complicated, since each of the ionization equilibria need to be accounted for simultaneously. However, for *weak polyprotic acids* the first ionization constant is much less than 1, and the second ionization constant is tiny compared with the first. For example, for carbonic acid the ionization constants are

$$K_{\mathrm{a1}} = 4.3 \times 10^{-7},$$

$$K_{\mathrm{a2}} = 4.8 \times 10^{-11}.$$

For such cases, we can treat the first ionization equilibrium as a weak acid with the result that, to a very good approximation,

$$[\mathrm{H_2A}] = \mathrm{c}_a$$

and

$$[\mathrm{H_3O^+}] = [\mathrm{HA^-}] = \sqrt{c_a\,K_{\mathrm{a1}}}\,.$$

Because the second ionization constant is so much smaller than the first, the second ionization *does not change appreciably either the concentration of H_3O^+ or HA^-*. That is, the values of these concentrations from the first ionization are used as the *equilibrium* values in the second ionization. The result is that

$$[\mathrm{A^{2-}}] = K_{\mathrm{a2}}\,.$$

> Show that this expression is correct if $K_{a1} \gg K_{a2}$.

For example, for a 0.100 M solution of carbonic acid, we have

$$[H_2A] = c_a = 0.100\,M,$$

$$[H_3O^+] = [HA^-] = \sqrt{c_a\,K_{a1}}\,.$$

> Show that $[H_3O^+] = [HA^-] = 2.1 \times 10^{-4}$ and that $[CO_3^{2-}] = 4.8 \times 10^{-11}$.

A neat consequence of this treatment of weak polyprotic acids is that it is simple to see how the concentration of the acid and its ionization products depends on pH. The first step is to rearrange the law of mass action for each ionization, as

$$\frac{[HA^-]}{[H_2A]} = \frac{K_{a1}}{[H_3O^+]}$$

and

$$\frac{[A^{2-}]}{[HA^-]} = \frac{K_{a2}}{[H_3O^+]}.$$

Next, we can define the *fractional concentrations*

$$f_0 = \frac{[H_2A]}{[H_2A] + [HA^-] + [A^{2-}]},$$

$$f_1 = \frac{[HA^-]}{[H_2A] + [HA^-] + [A^{2-}]},$$

and

$$f_3 = \frac{[A^{2-}]}{[H_2A] + [HA^-] + [A^{2-}]},$$

Then, we can use the equilibrium expressions for the successive ionization to relate fractional concentrations to one another as

$$f_1 = f_0\,\frac{K_{a1}}{[H_3O^+]} = f_0\,\frac{K_{a1}}{10^{\log_{10}([H_3O^+])}} = f_0\,K_{a1}\,10^{\mathrm{pH}}$$

and

$$f_2 = f_1\,\frac{K_{a2}}{[H_3O^+]} = f_1\,K_{a2}\,10^{\mathrm{pH}}.$$

> Show that these two relations are correct, by using the expressions for f_0, f_1 and f_2.

But also we know that the sum of the fractional concentrations is 1,

$$f_0 + f_1 + f_2 = 1$$

> Show that this expression is correct.

This means we have three equations for the three fractional concentrations, in terms of the acid ionization constants and the pH.

> Solve the three equations by hand to show that, at pH=7, the fractional concentrations are $f_1 = 0.19$, $f_2 = 0.81$ and $f_3 = 0.00039$.

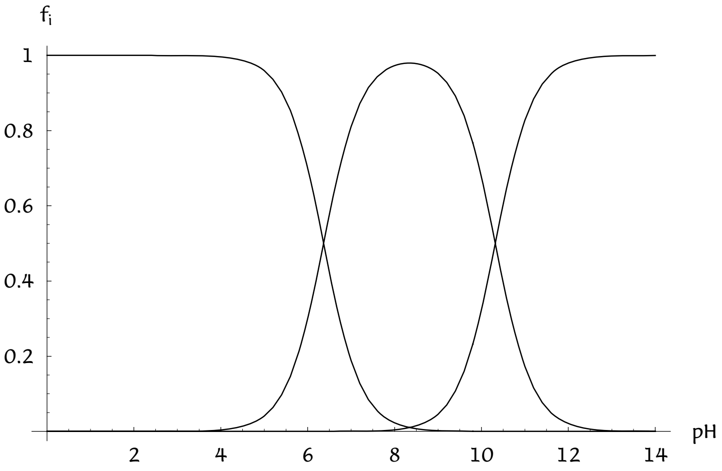
That is, the solution is 19% undissociated acid, 81% first ionization product, and 0.039% second ionization product. At pH = 11 the fractional concentrations are are $f_1 = 4.\times 10^{-6}$, $f_2 = 0.17$ and $f_3 = 0.83$; the distribution has changed completely, to 0.00040% undissociated acid, 17% first ionization product, and 83% second ionization product.

Here is how the distribution changes over the range of pH from 0 to 14.

pH	f_0	f_1	f_2
0	1.	4.3×10^{-7}	2.1×10^{-17}
1	1.	4.3×10^{-6}	2.1×10^{-15}
2	1.	0.000043	2.1×10^{-13}
3	1.	0.00043	2.1×10^{-11}
4	1.	0.0043	2.1×10^{-9}
5	0.96	0.041	$2.\times 10^{-7}$
6	0.7	0.3	0.000014
7	0.19	0.81	0.00039
8	0.023	0.97	0.0047
9	0.0022	0.95	0.046
10	0.00016	0.68	0.32
11	$4.\times 10^{-6}$	0.17	0.83
12	4.7×10^{-8}	0.02	0.98
13	4.8×10^{-10}	0.0021	1.
14	4.8×10^{-12}	0.00021	1.

Fractional amounts of H_2CO_3, HCO_3^- and CO_3^{2-} versus pH at 25°C.

and here is a graphical display of the changing fractional concentrations.



Fractional amounts of H_2CO_3(curve falls at high pH), HCO_3^- (curve peaks at middle pH values) and CO_3^{2-} (curve rises at high pH) versus pH at 25°C.

In solutions of just the polyprotic acid, the pH is fixed by the equilibrium equations. However, in the presence of buffers, the pH can be held at essentially arbitrary values. In this way the various fractions can be tuned to any desired values. Many biochemical processes depend on the acid fractions being particular values and buffer systems are adapted to maintain these values.