Acid Base Equilibrium

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1 Necessary Knowledge

- Understanding of equilibrium.
  - Understanding of equilibrium constant.
- Algebra.

2 Background

Acids and bases are relevant because they neutralize each other. That is, given an equal "amount" of equally "strong" acid and base, the two effectively cancel out (generally forming an inert salt, among other things). Given the acid Hydrochloric Acid and base Sodium Hydroxide, we have the following reaction.

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

This is a really useful property as no other chemical reaction outside of an Acid-Base reaction neutralizes. This can be written more generally for a given acid HA and base XOH in the following reaction.

$$HA_{(aq)} + XOH_{(aq)} \rightarrow AX_{(aq)} + H_2O_{(l)}$$

Arrhenius defined acids as a compound that contains hydrogen (HA) that dissociates (in water, it separates into hydrogen and other things). Arrhenius bases are compounds that contain hydroxide (XOH) that "release" the hydroxide in presence of water. The dissociation reactions are shown below.

$$HA_{(aq)} \rightarrow H^+_{(aq)} + A^-_{(aq)}$$

$$XOH_{(aq)} \rightarrow X^+_{(aq)} + OH^-_{(aq)}$$

However, the Arrhenius definition of acids and bases doesn't explain everything. In the definition, acids and bases *must* contain the ion they release. In practice, this isn't true because certain compounds *can* release the ions, but don't contain it.

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$$

In the above reaction, there is a neutralization reaction by the production of an inert salt ($NH_4CL_{(s)}$), but there are no Hydroxide (OH^-) ions in the reaction. To better explain these sorts of reactions, the primary (at least for the AP test[4]) acid and base theory is the Brønsted-Lowry definition.

3 Brønsted-Lowry and Conjugate Pairs

The Brønsted-Lowry definition of acids and bases is a bit more "loose" in the sense that more compounds can be acids or bases that did not fit into the Arrhenius definition. Any compound that exhibits the property of "releasing" hydrogen ion (H^+) is considered a Brønsted-Lowry acid; any compound that "takes" the hydrogen ion is considered a Brønsted-Lowry base.

3.1 Conjugate Pairs

One feature of the Brønsted-Lowry definition of acids and bases is the occurrence of conjugates. Like in math, conjugates are "counterparts" or "siblings" of sorts.

$$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$$

In the above reaction, Hydroflouric acid ($HF_{(aq)}$) donates/gives away a hydrogen ion (H^+) to become Flouride ion ($F^-_{(aq)}$); Dihydrogen Monoxide (or water! $H2O_{(l)}$) receives a hydrogen iron to form Hydronium ($H_3O_{(aq)}$). Due to this donation/reception relationship, Hydroflouric acid and Flouride ion are conjugate pairs. As per the definition of acids donating protons/hydrogen ions and bases receiving them, Hydrolouric acid is the acid and Flouride ion is the conjugate base.

Another way to analyze conjugate-pairs in an acid-base reaction is to isolate by element. If one chooses to look at compounds only containing Flourine, for example, one then has the following "reaction."

$$HF_{(aq)} \rightleftharpoons F^-_{(aq)}$$

In this case, one can see that the reactant, Hydroflouric acid ($HF_{(aq)}$) donates away its hydrogen ion to form the product, Flouride ion (F^-). Since Hydroflouric acid donated away its hydrogen ion, it is an acid. Since it forms Flouride ion, it is a conjugate base.

Likewise, water and Hydronium are, too, conjugate base pairs.

Conjugate pairs are when two species are related to each other by a difference of a single hydrogen ion/proton. In particular, species that differ by any larger multiple are not conjugate base pairs.[3]

3.1.1 Amphoteric Compounds

Substances that can act as both an acid and base are known as Amphoteric.

4 Measuring Acidity/Basicity

=Different acids and bases have different associated strengths. Acids such as Sulfuric acid (H_2SO_4) and Hydrochloric acid (HCl) are practically lethal in certain concentrations but some acids such as Acetic acid ($HC_2H_3O_2$) are consumable. In fact, Acetic acid is better known as vinegar. A similar situation exists in bases where bases can have a large range of strengths.

4.1 pH and pOH

- $p(anything) = -\log(anything)$
- $pH = -log[H^+]$
- $pOH = -log[OH^-]$
- $pK_a = -log[K_a]$

- $pK_b = -log[K_b]$

Since $-log(x)$ is a decreasing function, raising the concentration of hydrogen ion ($[H^+]$) will decrease the pH and vice-versa. In a solution of water the following properties hold.

- When $[H^+] = [OH^-]$, the solution is neutral and $pH = 7$.
- When $[H^+] > [OH^-]$, the solution is acidic and $pH > 7$.
- when $[H^+] < [OH^-]$, the solution is basic and $pH < 7$. [4]
- $pH + pOH = 14$.

4.2 Introduction to K_a and K_b

For a given dissociation acid reaction $HA \rightleftharpoons H^+ + A^-$, K_a is the equilibrium constant for that particular reaction.

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

Likewise, K_b for a given ionization base reaction $A^- + H_2O \rightleftharpoons HA + OH^-$, K_b is the equilibrium constant for that particular reaction.

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

Note that water (H_2O) is left out of the equilibrium constant expression since water is a liquid and has an unchanging concentration.

4.2.1 K_w

Observe the product of K_a and K_b

$$K_a \cdot K_b \Rightarrow \frac{[H^+][A^-]}{[HA]} \cdot \frac{[HA][OH^-]}{[A^-]}$$

$$\frac{[H^+]\cancel{[A^-]}}{\cancel{[HA]}} \cdot \frac{\cancel{[HA]}[OH^-]}{\cancel{[A^-]}} = [H^+][OH^-]$$

Notice that $[H^+][OH^-]$ is just the equilibrium constant for water.

$$K_a \cdot K_b = K_w$$

Since we have that $K_w = 1.0 \cdot 10^{-14}$, we have the following identities.

$$K_a \cdot K_b = 1.0 \cdot 10^{-14}$$

$$-\log(K_a \cdot K_b) = pK_a + pK_b = -\log(1.0 \cdot 10^{-14}) \Rightarrow pK_a + pK_b = 14$$

[1]

5 Acid Strength

Recall that the acidity of an acid relates to its pH and, thus, its concentration of Hydrogen ion ($[H^+]$) in solution at equilibrium. Beyond measure of pH, one qualifying measure of acidity is a notion known as "strength." Obviously, the stronger the acid, the more concentrated the Hydrogen ion is in solution in equilibrium and vice versa.

5.1 Strong Acids

Strong acids are essentially the "strongest" an acid may be. Literally all Hydrogen ion (H^+) in the compound dissociates/leaves the compound and enters the solution. That is, in the given acid dissociation reaction $HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$, all of the acid ($HA$) separates into its constituent ions and **none** of the acid is left over. The equilibrium expression does not exist since $K_a = \frac{[H^+][A^-]}{[HA]}$ ends up dividing by 0. Since the reaction completely finishes with no reverse reaction (since all of the reaction completes at complete dissociation/when all of the reactant is gone), the conjugate base is extremely weak, as nearly none of the reverse reaction happens. [4]

Strong bases take the same idea, but that all of the base completely ionizes such that no base is left over.

5.1.1 Notable Strong Acids

- HCl
- HBr
- HI
- HNO_3
- $HClO_4$
- H_2SO_4 [4]

5.1.2 Notable Strong Bases

- $LiOH$
- $NaOH$
- KOH
- $Ba(OH)_2$
- $Sr(OH)_2$ [4]

5.1.3 Example

Find the pH of a 0.010-molar solution of HCl. [4]

We have that the dissociation of Hydrochloric acid (HCl) in a reaction is given by the following reaction.

$$HCl \rightleftharpoons H^+ + Cl^-$$

Since Hydrochloric acid is a strong acid, all of the Hydorchloric acid dissociates to form hydrogen ions. That is, all 0.010-molar of Hydrochloric acid dissociates to form Hydrogen ion. Since for every 1 mole of Hydrochloric acid there is 1 mole of Hydrogen ion by the equation, we have that there is to be 0.010 molar of Hydrogen ion at completion.

Recall $pH = -log[H^+]$. Therefore, the pH of the solution is given below.

$$pH = -\log[H^+] \Rightarrow pH = -\log(0.010) \Rightarrow pH = 2$$

5.2 Weak Acids

Weak acids are the logical opposite of strong acids. Whereas strong acids completely dissociate into Hydrogen ion ($H+$) until there is no more of the compound left, weak acids don't completely dissociate. That is, only *some* of it dissociates into Hydrogen ion, and some of the original compound remains. Going back to K_a, the higher the concentration of Hydrogen ion, the greater the K_a (and lower the pK_a and pH) and thus the stronger the acid. Since not all of it dissociates at equilibrium, K_a is the key to discern concentration and its derived values.

5.2.1 Steps to Solve

1. Find the K_a or related value.
2. Write out balanced chemical equation and equilibrium expression.
3. Fill out ICE chart.
4. Solve.

5.2.2 Example

Find the pH of a 0.20 **molar solution of** $HC_2H_3O_2$ **if it has a** $K_a = 1.8 \cdot 10^{-5}$**.** [4]

Our first step is to write out the balanced chemical equation.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

From this, we can write our equilibrium expression.

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Now one sets up an ICE chart. It is constructed like so.

	$[HC_2H_3O_2]$	$[H^+]$	$[C_2H_3O_2]$
Initial	-	-	-
Change	-	-	-
Equilibrium	-	-	-

The question states the concentration of Acetic acid ($HC_2H_3O_2$) is 0.20 molar. In the beginning of the dissociation, when acetic acid is "put" into the beaker, there is only Acetic acid with none of its constituent ions. That is, there is no Hydrogen ion (H^+) or Acetate ion ($C_2H_3O_2^-$) in the beginning.

	$[HC_2H_3O_2]$	$[H^+]$	$[C_2H_3O_2]$
Initial	0.20	0	0
Change	-	-	-
Equilibrium	-	-	-

As per the balanced chemical equation, for every 1 mole of acetic acid there is 1 mole of hydrogen ion and acetate ion. This means that for every mole increase/decrease in acetic acid, there is an equal (but opposite) mole change in hydrogen ion and acetate ion. In this example, acetic acid dissociates, so the concentration must decrease and its constituent ions will thus increase. Both the increase/decrease will be an equal amount since the balanced chemical equation notes that each 1 mole change is followed by a 1 mole change.

	$[HC_2H_3O_2]$	$[H^+]$	$[C_2H_3O_2]$
Initial	0.20	0	0
Change	-x	+x	+x
Equilibrium	-	-	-

The values in the equilibrium table will just be the initial conditions after the change. That is, at equilibrium, acetic acid will be at $0.20 - x$ molar or its original concentration after being subtracted by some value. The same follows for its constituent ions, where it is no concentration then with values added.

	$[HC_2H_3O_2]$	$[H^+]$	$[C_2H_3O_2]$
Initial	0.20	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.20 - x$	x	x

Now that the equilibrium "concentrations" are known, or at least expressed, one can find the change in concentrations by the equilibrium expression. Since the equilibrium constant is equal to $1.8 \cdot 10^{-5}$ one has the following expression.

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \Rightarrow 1.8 \cdot 10^{-5} = \frac{x \cdot x}{(0.20 - x)} = \frac{x^2}{(0.20 - x)}$$

Solving, one finds that the change $x = 1.9 \cdot 10^{-3}$.

Since the equilibrium concentration of hydrogen ion is x, we have that the concentration of hydrogen ion at equilibrium is $1.9 \cdot 10^{-3}$.

Since $pH = -\log[H^+]$, we have the following expression.

$$pH = -\log[H^+] \Rightarrow pH = -\log(1.9 \cdot 10^{-3}) \Rightarrow pH = 2.7$$

5.3 Percent Dissociation/Ionization

Calculating percent dissociation/ionization is done by taking the concentration of either Hydrogen ion (H^+) for an acid or of Hydroxide (OH^-) divided by the original concentration of the acid/base.

Conceptually, the percent dissociation is a byproduct of acid/base strength. The stronger a given acid/base is, the more Hydrogen ion/Hydroxide there is at equilibrium, and thus, will have a higher percent dissociation/ionization at equilibrium.

Percent dissociation/ionization is also related to its concentration. Consider the situation with an acid dropped into water. If the acid is not very concentrated, there will be a relative abundance of water in comparison to the acid. With a large amount of water in respect to acid, it is easier for the water to interact with the acid than if there were less water. With a highly concentrated acid, there is less relative water, and so less ease to dissociate.

5.4 Analytically Determining Acid/Base Strength

Some questions state just acids/bases, with no numbers, and ask to compare/rank/etc the different acids/bases. This is done by observing the structure of each given acid/base.

5.4.1 Binary Acids

For acids that are composed of Hydrogen and another element, the less electronegative the other element is, the stronger the acid is. This is explained by bond length. The more electronegative an element is, the more the element will pull the electrons over. If it's extremely electronegative, dissociating (that is, ripping the hydrogen away) will be more difficult since it will be holding onto it more.

However, the opposite is true for ternary acids/oxoacids. The bond structure generally is Hydrogen linked to Oxygen, linked to another element. If the other element is very strong then that element will pull on the electrons; in doing so, electrons are pulled away from Hydrogen, weakening its bond. With a weaker bond, it is easier to dissociate/rip away, and will be thus a stronger acid. [4] [6]

5.5 Polyprotic Acids

Certain acids can repeat the dissociation process as the acids themselves contain multiple Hydrogen ions (H^+). In having more than one, the acids can give multiple away. Examples of polyprotic acids are H_2SO_4 and H_3PO_4.

Since the dissociation process can be repeated multiple times, there are multiple K_a values for each dissociation. In the example of H_2SO_4, there are two dissociation reactions, each with their own respective K_a values.

$$H_2SO_{4(aq)} \rightleftharpoons HSO^-_{4(aq)} + H^+_{(aq)}$$

$$K_{a_1} = \frac{[H^+][HSO_4^-]}{[H_2SO_4]}$$

$$HSO_4(aq)^- \rightleftharpoons H^+ + SO_4^{-2}$$

$$K_{a_2} = \frac{[H^+][SO_4^{-2}]}{[HSO_4^-]}$$

In particular, the first acid dissociation constant (K_{a_1}) is higher than the second (K_{a_2}) and so forth. This means the “first” acid will be the stronger than the “second” acid and so forth.

This is caused by the common ion effect, a consequence of Le Chatlier’s principle; The “second” acid can’t dissociate as easily because the first acid has already put in Hydrogen ion (H^+) into the solution, which will effectively “get in the way.”

5.5.1 Example

Find the concentrations of all compounds in a dissociation of $0.075M$ Hydrosulfuric acid. The equilibrium constants are given. $K_{a_1} = 1.0 \cdot 10^{-7}$ and $K_{a_2} = 9.1 \cdot 10^{-8}$. The first step is to write out the chemical equation for the first acid dissociation reaction.

$$H_2S_{(aq)} \rightleftharpoons HS^-_{(aq)} + H^+_{(aq)}$$

Using the balanced chemical equation, one then looks to create the ICE chart.

	$[H_2S]$	$[HS^-]$	$[H^+]$
Initial	0.075	0	0
Change	-x	+x	+x
Equilibrium	0.075-x	x	x

Using the balanced chemical equation, one then looks to express the equilibrium constant.

$$K_{a_1} = \frac{[HS^-][H^+]}{[H_2S]}$$

Then one equates the expression to the given K_a value.

$$K_{a_1} = \frac{[HS^-][H^+]}{[H_2S]} \Rightarrow 1.0 \cdot 10^{-7} = \frac{x \cdot x}{(0.075 - x)} = \frac{x^2}{0.075 - x}$$

$$x = 8.6 \cdot 10^{-5}$$
$$[H_2S] = 0.075 - x = 0.075 - (8.6 \cdot 10^{-5}) = 0.075M$$
$$[HS^-] = x = 8.6 \cdot 10^{-5}M$$
$$[H^+] = x = 8.6 \cdot 10^{-5}M$$

Next is to repeat the process with the second acid dissociation reaction.

$$HS^- \rightleftharpoons H^+ + S^{-2}$$

$$K_{a_2} = \frac{[H^+][S^{-2}]}{[HS^-]}$$

The important difference here is that the concentrations for Hydrogen ion ($[H^+]$) and Bisulfide ($[HS^-]$) are known. One can simply plug in the values for Hydrogen ion and Bisulfide and solve for the unknown concentration of Sulfide ion ($[S^{-2}]$).

$$K_{a_2} = \frac{[H^+][S^{-2}]}{[HS^-]} \Rightarrow 9.1 \cdot 10^{-8} = \frac{8.6 \cdot 10^{-5}[S^{-2}]}{8.6 \cdot 10^{-5}}$$
$$[S^{-2}] = 9.1 \cdot 10^{-8}$$

6 Neutralization Reactions

Recall that acids and bases have the unique property that an acid and a base will “neutralize.” In a reaction with an acid and a base, the two compounds will form water and an inert salt (a salt that doesn’t react further or anything). This water is produced by the Hydrogen H^+ and Hydroxide OH^- ions, which enter solution from the dissociation of the acid and base.

Chronologically, the acid and base in water will dissociate/ionize, releasing the its constituent elemental ion ($NaOH$, for example, would release both Na^+ as well as OH^-) as well as its Hydrogen/Hydroxide ion. Hydrogen and Hydroxide react to make water, the other ions will react to form a salt.

Specifically, a neutralization reaction has equal moles of acid and base. Since the product of concentration (“how much per space”) and volume (“amount of space”) produces moles (quantity, or “how much”), one can utilize this to obtain the following the formula.

$$n_a = M_a \cdot V_a; n_b = M_b \cdot V_b$$

$$n_a = n_b$$

$$M_a \cdot V_a = M_b \cdot V_b$$

Verbally, the formula for neutralization is “moles of acid times volume of acid equals moles of base times volume of base.”

Discerning the pH and related calculations for a given neutralization reaction depends on the strength of the acid and base.

6.1 Strong Acid - Strong Base Neutralization

When a strong acid reacts with a strong base, both of the compounds completely dissociate/ionize in the presence of water. The Hydrogen H^+ and Hydroxide OH^- ions will react to form water. At neutralization, the number of moles of both Hydrogen and Hydroxide ion will be equal, as will be the other ion in the acid/base. There will be no excess acid or base, only water and ions.

Since there is no excess acid or base, there is no excess Hydrogen or Hydroxide ion. As a result, the pH and pOH are both 7. [4]

6.2 Strong Acid - Weak Base

The strong acid will completely dissociate into ions in the presence of water; the hydrogen ion H^+ will be donated to the weak base. As per the donation of a single proton, the product is the strong acid's conjugate base. [4]

$$HCl_{(aq)} + NH_{3(aq)} \rightleftharpoons NH_4Cl_{(aq)}$$

$$H^+ + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)}$$

Note that the Chloride ion (Cl^-) disappears, as it is a spectator ion in the reaction.

6.3 Weak Acid - Strong Base

The strong base will completely ionize in water, existing as its constituent ion and Hydroxide ion (OH^-). For example, the strong base $NaOH$ would "dissociate" into Sodium ion (Na^+) and Hydroxide ion (OH^-). The Hydroxide ion then reacts with the weak acids Hydrogen ion (H^+) to produce water. [4]

$$HC_2H_3O_{2(aq)} + NaOH_{(aq)} \rightleftharpoons H_2O_{(l)} + NaC_2H_3O_{2(aq)}$$

$$HC_2H_3O_{2(aq)} + OH^- \rightleftharpoons H_2O_{(l)} + C_2H_3O_2^-$$

Note that the Sodium ion (Na^+) disappears, as it is a spectator ion in the reaction.

6.4 Weak Acid - Weak Base

In this reaction, the weak acid, that partially dissociates, donates its Hydrogen (H^+) ion to the weak base, which accepts said proton. [4]

$$HC_2H_3O_{2(aq)} + NH_{3(aq)} \rightleftharpoons C_2H_3O^-_{2(aq)} + NH_{4(aq)}$$

6.5 Discerning pH of Neutralization

In neutralization reactions, all of the Hydrogen ion (H^+) from the acid dissociates and reacts with the base. To find the pH of the solution at neutralization, one makes use of an ICE chart. Instead the table's values being filled with concentrations, the table is filled with moles.

35.0 mL of 1.5 M HCN, a weak acid ($K_a = 6.2 \cdot 10^{-10}$) is mixed with 25.0 mL of 2.5 M KOH. Calculate the pH of the final solution. [4]

As a weak acid - strong acid reaction, the net ionic is the weak acid reacting with Hydroxide (OH^-) ion to form water while dissociating its constituent ion.

$$HCN_{(aq)} + OH^- \rightleftharpoons H_2O_{(l)} + CN^-$$

	HCN	OH^-	CN^-
Initial	-	-	-
Change	-	-	-
Equilibrium	-	-	-

In order to calculate the initial concentrations, one multiplies the molarity ("how much per how much space") by the volume ("how much space") of the compound.

$$35.0\text{mL HCN} \cdot \frac{1\text{L HCN}}{1000\text{mL HCN}} \cdot \frac{1.5\text{m HCN}}{1\text{L HCN}} = 0.052\text{m HCN}$$

$$25.0\text{mL KOH} \cdot \frac{1\text{L KOH}}{1000\text{mL KOH}} \cdot \frac{2.5M\text{m KOH}}{1\text{L KOH}} \cdot \frac{1\text{m OH}^-}{1\text{m KOH}} = 0.062\text{m OH}^-$$

	HCN	OH^-	CN^-
Initial	0.052m	0.062m	0
Change	-	-	-
Equilibrium	-	-	-

Observe that in presence of water, HCN dissociates. For each mole of HCN that dissociates, there is an equal increase in the number of moles of CN, and an equal decrease in OH. This is verified as per the balanced chemical reaction, where such changes mirror a 1-to-1 mole ratio.

More importantly, the reaction will continue to run until there is no Hydrogen remaining. Since the source of Hydrogen in this reaction is that of HCN, all of HCN will be used up. That is, the change will be the same number of moles in the initial number of moles. Since the changes in Hydroxide and CN will be the same amount, the change, too, will be the initial number of moles of HCN.

	HCN	OH^-	CN^-
Initial	0.052m	0.062m	0
Change	-0.052m	-0.052m	+0.052
Equilibrium	0	0.010m	0.052m

From this, one concludes that the number of Hydroxide ions in solution is 0.010m. Since $pOH = -\log[OH^-]$, the next step is to find the concentration of Hydroxide ion. Concentration is quantity divided by volume; in the question, there is 35.0 mL of a weak acid and 25.0 mL of the base. There is a combined volume of 60.0 mL. Then to find concentration, one divides the number of moles by the combined volume.

$$\frac{0.010m}{0.060L} = 0.17m$$

$$pOH = -\log[OH^-] = -\log(0.17m) = 0.76$$

$$pH + pOH = 14 \Rightarrow pH + 0.76 = 14 \Rightarrow pH = 13.24$$

6.6 Henderson-Hasselbach

The prior example demonstrates how to discern the pH of a neutralization reaction where a strong acid or base (specifically KOH) was in excess. That is, there were more moles of the strong base than there were the acid. However, if the weak acid or base is in excess, it is often easier to use the Henderson-Hasselbach equation.

$$pH = pK_a + log\frac{[A^-]}{[HA]}$$

$[A^-]$ refers to the concentration of the conjugate base, and $[HA]$ is the concentration of the acid.

$$pOH = pK_b + log\frac{[HB^+]}{[B]}$$

$[HB^+]$ refers to the concentration of the conjugate acid, and $[B]$ is the concentration of the base.

25.0 mL of 1.0 M HCl is mixed with 60.0 mL of 0.50 M Pyridine (C_5H_5N), a weak base ($K_b = 1.5 \cdot 10^{-9}$). Determine the pH of the solution. [4]

The first step is to write out the balanced chemical equation for the neutralization.

$$HCl_{(aq)} + C_5H_5N_{(aq)} \rightleftharpoons HC_5H_5N^+ + Cl^-$$

Removing the spectator Chloride (Cl^-) ion from the chemical reaction results in the net ionic reaction.

$$H^+ + C_5H_5N_{(aq)} \rightleftharpoons HC_5H_5N^+$$

The next step is to construct the ICE chart, remembering that the values in the table are the quantity of moles.

	H^+	C_5H_5N	HC_5H_5N
Initial	-	-	-
Change	-	-	-
Equilibrium	-	-	-

To find the initial quantity of the compounds, one multiplies the concentration by the volume.

$$25.0\text{mL HCl} \cdot \frac{1\text{L HCl}}{1000\text{mL HCl}} \cdot \frac{1.0\text{m HCl}}{1\text{L HCl}} \cdot \frac{1\text{mol H}^+}{1\text{mol HCl}} = 0.025\text{mol H}^+$$

$$60.0\text{mL}C_5H_5N \cdot \frac{1\text{L}C_5H_5N}{1000\text{mL}C_5H_5N} \cdot \frac{0.50\text{m}C_5H_5N}{1\text{L}C_5H_5N} = 0.030\text{mol}C_5H_5N$$

	H^+	C_5H_5N	HC_5H_5N
Initial	0.025	0.030	0.000
Change	-	-	-
Equilibrium	-	-	-

Since Pyridine (C_5H_5N) ionizes in the presence of water as per the balanced chemical equation, there is a one-to-one mole ratio between the reactants and products. That is, for every one mole of Hydrogen ion (H^+) and Pyridine reacts, exactly one mole of Pyridine cation (HC_5H_5N) is produced. This reaction will continue until there are no more moles of Hydrogen ion to donate to the base. That is, the change in Hydrogen ion, and thus Pyridine as well, will be the same as the initial quantity of Hydrogen ion.

	H^+	C_5H_5N	HC_5H_5N
Initial	0.025	0.030	0.000
Change	-0.025	-0.025	+0.025
Equilibrium	-	-	-

Then one sums the initial and change values for the quantities at equilibrium.

	H^+	C_5H_5N	HC_5H_5N
Initial	0.025	0.030	0.000
Change	-0.025	-0.025	+0.025
Equilibrium	0	0.005	0.025

With the quantities of the compounds at equilibrium, one then divides by the total volume to discern the concentrations of the compounds at equilibrium. The total volume is the sum of the volumes. These concentrations are the concentrations of the conjugate acid and the base, used in the Henderson-Hasselbach equation.

$$25.0\text{mL} + 60.0\text{mL} = 85.0\text{mL}$$

$$[C_5H_5N] = \frac{0.005\text{mol Pyridine}}{0.085\text{L}} = 0.059M$$

$$[HC_5H_5N] = \frac{0.025\text{mol Pyridine Cation}}{0.085\text{L}} = 0.29M$$

Then the pOH is found through the Hendersen-Hasselbach equation.

$$pOH = pK_b + log\frac{[HB^+]}{[B]}$$

$$pOH = -\log(1.5 \cdot 10^{-9}) + \log(\frac{0.29M}{0.059M})$$
$$pOH = 9.5$$
$$pH + pOH = 14$$
$$pH + 9.5 = 14$$
$$pH = 3.5$$

7 Buffers

Buffers are solutions that, when acids or bases are added to, can “resist” changes in pH and hold it stable. Consider adding drops of a strong acid such as Hydrochloric acid to a solution of, say, water. As per the acids strength (it being a strong acid), the pH would dramatically fall as the acid dissociates and releases Hydrogen ion into water. In contrast, a buffer’s pH would only decrease a relatively smaller amount; the same thought process applies reversely to strong bases, where adding a strong base to a buffer solution would not change the pH solution as much as adding a strong base to water. [2]

Buffer solutions are composed with either a weak acid and its conjugate base, or a weak base and its conjugate acid. The more added equates to a larger amount of acid/base being ”absorbed” by the solution. The acid/base and its conjugate are able to remain in solution as per the common ion effect. In solution, the chemical reaction attempts to keep the quantities of the two constant, at equilibrium. [5]

7.1 Mechanics

Consider a buffer solution composed of acetic acid ($HC_2H_3O_2$) and a compound with its conjugate base, Sodium acectate ($NaC_2H_3O_2^-$). The equilibrium reaction in water is given by the following.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

Then one adds the compound with its conjugate base

$$NaC_2H_3O_2 \rightleftharpoons C_2H_3O_2^- + Na^+$$

If a strong acid is added into the solution, the acid will dissociate into Hydrogen ion and its constituent ion. These hydrogen ion entering solution, instead of going straight into solution and directly affecting the concentration of hydrogen ion, will instead (at least somewhat) react with the acetate ion ($C_2H_3O_2^-$). In doing so, the change in concentration will be somewhat subdued.

Likewise, adding in a strong base with ionize and produce Hydroxide (OH^-) ion in solution. These will then bond with the positively charged Sodium ion (Na^+); only some of the hydroxide will go into solution, changing the pOH and thus the pH less so.

7.2 Example

What is the pH of a buffer solution with concentrations of 0.20 M $HC_2H_3O_2$ and 0.50 M $C_2H_3O_2^-$? $K_a = 1.8 \cdot 10^{-5}$ [4]

This is a simple matter of using the Henderson-Hasselbach formula.

$$pH = Pk_a + \log \frac{A^-}{HA}$$
$$pH = -\log 1.8 \cdot 10^{-5} + \log 0.50M0.20M$$
$$pH = 5.1$$

Notice by inspection that if $[A-] = [HA]$, that $pH = pK_a$, since $\log(1) = 0$. When choosing a buffer for a solution, it’s best to choose a buffer solution such that $pH = pK_a$ as closely as possible.

8 Indicators

Indicators are substances added to solutions that make the titration process easier. Most acids and bases are colorless, making it impossible to discern when a titration has "ended" without a pH meter or such. Instead, indicators change color when the titration has completed, or around it. Indicators are weak acids that change color in reference to the equivalence point by means of Le Chatlier's principle. Indicators have the following equilibrium expression.

$$H(IN) \rightleftharpoons H^+ + (IN)^-$$

$$K_a = \frac{[H^+][IN^-]}{[H(IN)]}$$

The acid itself $[H(IN)]$ and ion IN are different colors.

Consider the existence of excess acid (in the case of titrating a base with an acid past the equivalence point). The additional Hydrogen (H^+) ion that dissociates from the ion will, by Le Chatlier's principle, produce more $H(IN)$, decreasing the quantity IN, changing the solution's color from whatever IN's is, to the other. The reverse color change occurs with excess base, where the diffency of Hydrogen ion will lead to the production of $(IN)^-$ and decrease in the quantity of $H(IN)$.

The indicator has its color change when the concentrations of the acid and its ion are at equal concentrations. This gives the following equilibrium expression.

$$K_a = \frac{[H^+]\cancel{[IN^-]}}{\cancel{[H(IN)]}}$$

$$K_a = [H^+]$$

$$pK_a = pH$$

For a given titration, the ideal indicator has its $pK_a = pH$ as close as possible.

9 Titrations

"Neutralization reactions are generally performed by titration, where a base of known concentration is slowly added to an acid (or vice versa). The progress of a neutralization reaction can be shown in a titration curve." [4]

For a titration of a strong acid with a strong base or vice-versa, the pH change is slow at first until at the equivalence point, where it spikes dramatically. After the equivalence point, the pH change slows down and levels off.

For a titration of a weak acid with a strong base or strong acid with a weak base or vice versa, the pH change is fast at first, then slows down into a buffer region, before spiking at the equivalence point, leveling off again.

9.1 Heuristics

If the starting solution is an acid, the pH will be less than 7 as the solution is acidic. If the starting solution is a base, the pH will be greater than 7 as the solution is basic.

The "position" of the equivalence point depends on the relative strengths of the titrating compounds. If it's a strong acid/strong base titration, the equivalence point will be at $pH = 7$. If one of te compounds is strong with the other weak, the equivalence point will be on the side of the stronger compound. That is, a strong acid/weak base titration will have a pH at the equivalence point less than 7; a weak acid/strong base titration will have a pH at the equivalence point greater than 7.

10 Example

20.0 mL of .100 M NH_3 is titrated with 0.050 M HCl. $K_b = 1.8 \cdot 10^{-5}$

10.1 Starting pH

This is done by constructing an ICE chart of the starting compound, then solving to find the concentration of either Hydrogen ion $[H^+]$ or Hydroxide ion $[OH^-]$.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

	NH_3	NH_4^+	OH^-
Initial	0.100	0	0
Change	-x	+x	+x
Equilibrium	0.100-x	x	x

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

$$1.8 \cdot 10^{-5} = \frac{x^2}{0.100 - x}$$

$$x = 0.00134M$$

$$[OH^-] = x = 0.00134M$$

$$pOH = -\log[OH^-] = -\log(0.00134M) = 2.87$$

$$pH + pOH = 14 \Rightarrow pH = 14 - 2.87 \Rightarrow pH = 12.11$$

10.2 Volume at Equivalence Point

This is found through $M_a \cdot V_a = M_b \cdot V_b$ or stoicheometry.

$$M_a \cdot V_a = M_b \cdot V_b$$

$$V_a = \frac{M_b \cdot V_b}{M_a}$$

$$V_a = \frac{0.10\text{mol} \cdot 20\text{mL}}{0.05\text{mol}}$$

$$V_a = 40\text{mL}$$

10.3 Half-Equivalence Point

The volume at the half-equivalence point is given by half the volume of the equivalence point, hence its name.

$$V_{\frac{1}{2}\text{eq}} = \frac{V}{2} = \frac{40\text{mL}}{2} = 20\text{mL}$$

At the half-equivalence point, $pH = pK_a$

$$pH = pK_a$$

$$pOH = pK_b = -\log 1.8 \cdot 10^-5 = 4.74$$

$$pH + pOH = 14 \Rightarrow pH = 14 - 4.74 = 9.26$$

10.3.1 pH at Equivalence Point

The first step is to write the dissociation/ionization of the conjugate compound reacting with water.

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

Then the next step is to construct the ice chart for the given reaction.

	NH_4^+	H_3O	NH_3^+
Initial	-	-	-
Change	-	-	-
Equilibrium	-	-	-

To find the concentration of NH_4^+, one uses stoicheometry of the volume at the equivalence point, converting to molarity by dividing by the total volume (titrant volume added to the initial volume).

$$0.040L \cdot \frac{0.1\text{M NH}_3}{1\text{L NH}_3} \cdot \frac{1}{0.060\text{L}} = 0.033\text{M}$$

	NH_4^+	H_3O	NH_3^+
Initial	0.033	0	0
Change	-x	+x	+x
Equilibrium	0.033-x	x	x

Using the identity $K_a \cdot K_b = K_w = 1.0 \cdot 10^{-14}$, one can find K_a from K_b.

$$K_a = \frac{1.0 \cdot 10^{-14}}{K_b} = \frac{1.0 \cdot 10^{-14}}{1.8 \cdot 10^-5} = 5.56 \cdot 10^{10}$$

$$K_a = \frac{[H_3O^+][NH_3^+]}{[NH_4^+]}$$

$$5.56 \cdot 10^{10} = \frac{x^2}{0.033 - x}$$

$$x = 4.28 \cdot 10^{-6} M$$

$$[H^+] = [H_3O^+] = x = 4.28 \cdot 10^{-6}$$

$$pH = -\log[H^+] = -\log(4.28 \cdot 10^{-6}) = 5.4$$

10.4 pH at a Point After Equivalence Point

Pick a certain volume greater than the equivalence point. In this case, it will be 10mL greater than the equivalence point for $10mL + 40mL = 50mL$. Using stoicheometry, convert the amount of volume greater than the equivalence point to moles of solution.

$$0.010L \cdot \frac{0.5\text{mol HCl}}{1\text{L HCl}} = 0.005\text{mol HCl}$$

Then, to find the concentration of the compound, one divides by the total volume at the given point.

$$\frac{0.005\text{mol HCL}}{0.070\text{L HCl}} \cdot \frac{1\text{mol H}^+}{1\text{mol HCl}} = 0.007144\text{M H}^+$$

$$pH = -\log[H^+] = -\log(0.007144\text{mol H}^+) = 2.1$$

10.5 Polyprotic Acids

Acids that have multiple Hydrogen ions to give away have "multiple" titration curves stacked on one another. The half-equivalence points are given by the pK_as for each "acid." The same process applies for each "special" point, simply substituting in different values for each volume/molarity.

References

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[6] Shmoop Editorial Team. Chemistry properties that determine acid strength - shmoop chemistry.