Chapter 14 – Acid-Base Equilibria

Most solutions that occur in nature are slightly acidic. One reason for this is that when carbon dioxide dissolves in water, it forms carbonic acid, H_2CO_3. Basic solutions that exist in nature typically have limited direct exposure to air. For example, your blood is slightly basic and, under ideal circumstances, is not open to the air. Likewise, peach pits contain strychnine, an organic base, which is not protonated because of the shell that seals out the atmosphere. Figure 14.2 (p. 769) lists the pHs of some common substances. Note that only seawater occurs openly in nature with a pH over 7. We'll see why before this chapter is through.

14.1   Brønsted-Lowry Acids and Bases

Earlier, in Chapter 2, you were given quick working definitions of acids and bases. We will now expand on those definitions, but begin with a short reminder of how acids and bases were originally identified and characterized.

Acidic solutions generally have a sour taste (e.g. grapefruit and lemon juices) and dissolve certain metals. Bases have a bitter taste and feel slippery. The slippery feeling comes from the base breaking down oils and fatty acids in your hands. The old lye soap used a century ago cleaned by removing the top layer of skin and anything that was attached to it. Modern soaps use a different type of active chemical that doesn't react with your skin.

The first good definition of acids and bases was proposed by Arrhenius (the same person who proposed activation energy). He proposed that acids were substances that produces H^+ ions in water and bases were substances that produces OH^- ions in water. However, this definition turns out to be too restrictive because it requires the presence of water.

The hydrogen ion, H^+, is nothing but a proton and can't really exist freely in aqueous solution

because of its high charge density. The positive charge attracts the lone pairs of electrons on nearby water molecules. The result is that each proton is surrounded by water molecules with their lone pair electrons pointing at the proton. Typically, 3 to 4 water molecules associate with each proton ($H(H_2O)_3^+$ or $H(H_2O)_4^+$), but the hydrogen ion is usually written as either $H^+_{(aq)}$ or $H_3O^+_{(aq)}$ for simplicity's sake. The latter form indicates the association of water with the proton and is called the hydronium ion.

In 1923, two chemists Johannes Brønsted and James Lowry independently proposed new definitions of acids and bases. They proposed an acid is a substance that donates a proton to another substance. A base is something that can accept a proton from another substance. These definitions have a couple of significant advantages over the older Arrhenius definitions. First some compounds (such as alcohols) clearly acted like acids some of the time, but did not qualify under the Arrhenius definition. For this reason, all Arrhenius acids and bases are also Brønsted-Lowry acids and bases (but not *vice-versa*). Second, it included reactions that occur in non-aqueous solutions. For example, the gas phase reaction

$$HCl_{(g)} + NH_{3\,(g)} \rightarrow NH_4Cl_{(s)}$$
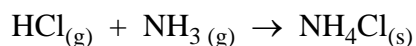
is a Brønsted-Lowry acid/base reaction, but not an Arrhenius acid/base reaction. Brønsted-Lowery acid/base reactions are frequently called "proton-transfer" reactions because of the descriptive nature of the term.

Some compounds possessing both a polar element-to-hydrogen bond (e.g. O-H or N-H) and a lone pair of electrons frequently are able to donate a proton or accept one depending on the conditions (water provides an example of this behavior). Molecules that can act both as an acid and base are called amphoteric. For example, water reacts with hydrogen chloride gas to yield hydronium and chloride ions:
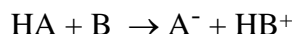
$$H_2O_{(\ell)} + HCl_{(g)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$
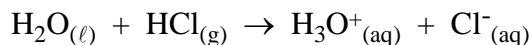
It also reacts with ammonia to yield ammonium and hydroxide ions:

$$H_2O_{(\ell)} + NH_{3\ (g)} \rightarrow NH_4^+_{(aq)} + OH^-_{(aq)}$$
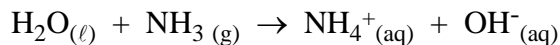
Conjugate Acid-Base Pairs

In an acid-base reaction, a proton is transferred from the acid to the base.

$$HA + B \rightarrow A^- + HB^+$$

The base that received the proton can now donate that proton to something else. It has become an acid. Likewise, the acid that donated the proton can now accept one from somewhere else. It has

Example: $HCl + H_2O \longrightarrow Cl^- + H_3O^+$
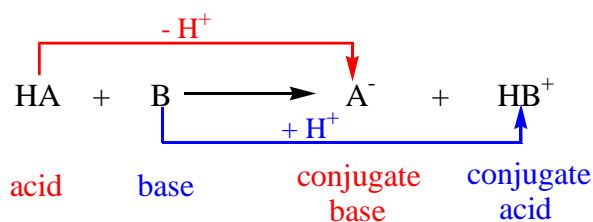
become a base. The new base and acid from which it was formed are called a conjugate acid/base pair. Analogously, the new acid and the base from which it was formed are also a conjugate acid/base pair. Every Brønsted-Lowry acid has a conjugate base and every Brønsted-Lowry base has a conjugate acid.

Relative Strengths of Acids and Bases

When writing an acid/base reaction, the direction of the arrow tells us something important. The stronger is an acid or base, the weaker is its conjugate. Consider hydrogen chloride and water. If hydrogen chloride is the stronger acid, then it is better at giving up H^+ ions than H_2O. If this is true, then chloride ion in HCl must be poorer at holding onto its H^+ than H_2O in H_3O^+. Hence, chloride ion is the weaker base and is the conjugate base of hydrogen chloride. We'll go over how
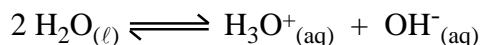
they are mathematically related in a few pages.

When strong acids dissolve in water, they completely transfer their protons to water molecules to form hydronium ions as shown above. Thus, the strongest acid that can exist in water is H_3O^+. This is called the <u>leveling effect</u>. Similarly, the strongest base that can exist in water is hydroxide ion. Bases stronger than hydroxide will remove a proton from water to form hydroxide ion. To develop a solution that is more strongly acidic than a strong acid in water, the strong acid must be dissolved in a more acidic solvent (e.g. HCl in acetic acid). Likewise, dissolving a strong base in a less acidic solvent than water generates a more strongly basic solution (e.g. NaOH in ethanol).

When acids and bases react, the position of the equilibrium favors transfer of a proton from the stronger acid to the stronger base. Thus, for the reaction:

$$HA + B \rightarrow A^- + HB^+$$
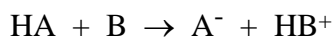
there are two acids (HA and HB^+) and two bases (B and A^-). The stronger acid will yield the weaker conjugate base. Thus, all you need to do is identify the stronger of one of the pairs to determine the direction of reaction.

The poor electrical conductivity of very pure water surprises most people. So why is water a poor conductor? Because it contains very few ions. In contrast, tap water is a good electrical conductor because it contains dissolved salts. You've probably seen this when you let water evaporate from a spoon or glass when it is drying. There are a few dissolved ions in pure water though and this provides water with what little conductivity it displays. To produce those ions, water undergoes an interesting reaction called <u>autoionization</u>, in which it reacts with itself to form ions.

$$2\ H_2O_{(\ell)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

or, more commonly,

$$H_2O_{(\ell)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

The former reaction is more representative of what actually happens in solution. The lone pair of electrons on one water molecule is attracted to, then removes, a hydrogen atom on a neighboring water molecule. Since this is an equilibrium, there must be an equilibrium constant associated with it.

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]} = \frac{[H^+][OH^-]}{[H_2O]}$$

Usually H_3O^+ is expressed as H^+ in these equilibrium expressions to make writing them easier. Now, water is a pure substance and has a fixed concentration at any given temperature just like the solids presented in the previous chapter, thus:

$$K_{eq}[H_2O] = [H^+][OH^-] = K_w$$

K_w is called the <u>ion-product constant for water</u> and has a value of 1.0 x 10^{-14} at 25 ºC. You will need to memorize this number. In pure water, at 25 ºC: $[H^+] = [OH^-] = 1.0$ x 10^{-7} M (see Exercise 16.4, p. 621). This very low concentration of ions accounts for the low conductivity described above for water.

14.2   <u>pH and pOH</u>

Water in which $[H^+] = [OH^-]$ is called <u>neutral</u>. (It is important to remember that when an acid or base is "neutralized" the final solution need not be neutral. We'll return to this later.)   When $[H^+] > [OH^-]$, the water is <u>acidic</u>. When $[H^+] < [OH^-]$, the water is <u>basic</u>. For example, you've worked with 0.1 M $HCl_{(aq)}$ in lab before. As you know, hydrochloric acid is a strong acid and ionizes completely in water. Therefore, $[H^+] = [HCl] = 0.1$ M.

$$1.0 \text{ x } 10^{-14} = [H^+][OH^-]$$

$$1.0 \text{ x } 10^{-14} = (0.1)[OH^-]$$

$$[OH^-] = 1.0 \text{ x } 10^{-13} \, M$$

As with all equilibrium constants, K_w has no units so the units on $[H^+]$ are discarded and then units for $[OH^-]$ are inserted when necessary.

Since the hydrogen ion concentration in water is typically quite small, the pH scale was developed to simplify the expression of how acidic or basic a solution is. It is a logarithmic scale and so eliminates the exponential term.

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

The pH of pure water at 25 °C is calculated as:

$$pH = -\log(1.0 \text{ x } 10^{-7}) = 7.00$$

There are a few points worth noting here. First, pH = 7.00 is neutral only at 25 °C, but unless you are told otherwise, all of the examples you will see in this book will be at 25 °C. Next, only the zeros are significant. The "7" provides information on the exponent. By convention, pHs are written with only two digits right past the decimal. Be very careful with significant figures here. A pH of 6.31 has only two significant digits. Remember, this is a logarithmic scale. This means that a change in pH of one unit equals a concentration change of a factor of 10! For that reason, in biological systems pH ranges are usually relatively small (on the order of a few tenths of a pH unit). Larger pH changes can cause cell, and even organism, death.

pH decreases as $[H^+]$ increases. Therefore:

in acidic solution $[H^+] > 1.0 \text{ x } 10^{-7}$ and pH < 7.00

in basic solution $[H^+] < 1.0 \text{ x } 10^{-7}$ and pH > 7.00

A similar scale exists for hydroxide ion, not surprisingly called the pOH scale. It is calculated according to the equation:

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

pH and pOH are related according to an equation derived below.

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

$$-\log([H^+][OH^-]) = -\log(1.0 \times 10^{-14})$$

$$-\log[H^+] - \log[OH^-] = 14.00$$

$$pH + pOH = 14.00$$

14.3   Relative Strengths of Acids and Bases

Acid and Base Ionization Constants

Remember that a strong acid completely ionizes. Thus, the $[H^+]$ equals the concentration of the added acid before ionization. You should remember the most common strong acids: HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4. (Only the first proton in H_2SO_4 completely ionizes.) Assume all other acids you encounter in this class to be weak acids.

Example: What is the pH of 0.20 M $HClO_4$?

$$[H^+] = [HClO_4] = 0.20 \ M$$

$$pH = -\log(0.20) = 0.70$$

Strong Bases

Strong bases can be thought about like strong acids. They dissociate completely, however since some bases produce more than one OH^-, their concentrations do not necessarily equal the hydroxide concentration (e.g. $Mg(OH)_2$). All Group IA and IIA metal hydroxides are strong bases, except beryllium hydroxide, $Be(OH)_2$. Many weak bases that contain protons become strong bases when deprotonated. For example, ammonia is a weak base, while NH_2^- is a strong base.

$$NH_2^-{}_{(aq)} + H_2O_{(\ell)} \rightarrow NH_3{}_{(aq)} + OH^-{}_{(aq)}$$
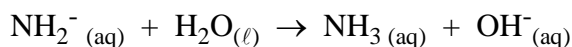
Sodium hydroxide and potassium hydroxide are the most commonly used strong bases. This is because the other alkali metal bases are more expensive and the alkaline earth bases have low solubilities.

Furthermore, just because a strong base is dissolved, it doesn't mean the solution is strongly basic. This is because many strong bases are poorly soluble in water. Remember from Chapter 11, the example of Milk of Magnesia where $Mg(OH)_2$ is a strong electrolyte/base, but is very poorly water soluble so you can drink it without damaging your mouth or throat.

Example: What is the pH of 0.20 M barium hydroxide?

$$[OH^-] = (0.20\ mol_{Ba(OH)2})\left(\frac{2\ mol_{OH-}}{1\ mol_{Ba(OH)2}}\right) = 0.40\ M$$

$$pOH = -\log(0.40) = 0.40$$

$$pH = 14.00 - 0.40 = 13.60$$
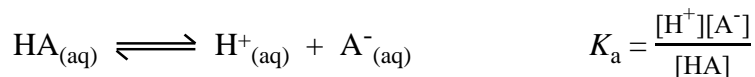
or

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.40} = 2.5 \times 10^{-14}\ M$$

$$pH = -\log(2.5 \times 10^{-14}) = 13.60$$

Weak Acids

Most acids are weak acids and exist as an equilibrium in water between their protonated (acid) form and deprotonated (conjugate base) form. When the equilibrium is written out, the transfer of the proton to water is usually written as a simple loss of a proton for clarity.

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

where K_a is the acid-dissociation constant. The larger is K_a, the stronger is the acid.

Example: A 0.10 M formic acid (HCO_2H) solution has a pH of 2.38. What is its K_a? What is its

percent ionization?

a) $[H^+]$ = antilog(-2.38) = 4.2 x 10^{-3} M (Note: The number of significant figures is correct.)

Since we assume the only source of H^+ ions is the acid, then $[HCO_2^-]$ = $[H^+]$.

Finally, $[HCO_2H]_i$ = 0.10 M.

So $[HCO_2H]_e$ = 0.10 M – 0.00420 $M \approx$ 0.10 M

$$K_a = \frac{(4.2 \times 10^{-3})(4.2 \times 10^{-3})}{0.10} = 1.8 \times 10^{-4}$$

b) % dissociation = $\dfrac{[H^+]_e}{[HCO_2H]_i}$ x 100% = $\dfrac{4.2 \times 10^{-3}}{0.10}$ x 100% = 4.2 %

Calculate K_a from pH

This section is basically a demonstration of how to calculate the pH of a weak acid solution given the initial concentration of the acid and its K_a. Consider two acetic acid (CH_3CO_2H or HOAc) solutions (0.0030 M and 3.0 M). We will calculate their pHs and percents dissociation.

There is a useful mathematical tool that comes into play in these problems. If the initial acid concentration is more than 100 times K_a, the amount of acid that dissociates is negligible and can be ignored when calculating the undissociated acid concentration. If you make this approximation, you **must** check your final answer to verify its validity.

$$HOAc \rightleftharpoons H^+ + OAc^- \qquad K_a = \frac{[H^+][OAc^-]}{[HOAc]} = 1.8 \times 10^{-5}$$

3.0 M: $[HOAc]_i$ = 3.0 M $\qquad\qquad$ $[HOAc]_e$ = 3.0 – x M

$[H^+]_i$ = $[OAc^-]_i$ = 0 M $\qquad\qquad$ $[H^+]_e$ = $[OAc^-]_e$ = x M

$$1.8 \times 10^{-5} = \frac{x^2}{3.0 - x}$$

Since $[HOAc]_i > 100K_a$, assume $3.0 - x \approx 3.0$.

$$1.8 \text{ x } 10^{-5} = \frac{x^2}{3.0}$$

$x = 7.3 \text{ x } 10^{-3}$

check: $3.0\ M - 0.0073\ M = 2.9927 \approx 3.0$. The assumption is valid.

$pH = -\log(7.3 \text{ x } 10^{-3}) = 2.13$

$$\% \text{ dissociation} = \frac{7.3 \text{ x } 10^{-3}M}{3.0\ M} \text{ x } 100\% = 0.24\ \%$$

0.0030 *M*: $[HOAc]_i = 0.0030\ M$ $[HOAc]_e = 0.0030 - x\ M$

$[H^+]_i = [OAc^-]_i = 0\ M$ $[H^+]_e = [OAc^-]_e = x\ M$

$$1.8 \text{ x } 10^{-5} = \frac{x^2}{0.0030 \text{ - } x}$$

Now $100K_a \approx [HOAc]_i$ so assuming x is negligible might not work. There are two ways to go about solving the problem here. The straightforward way is to use the quadratic equation (which is left to you). The following is an alternative approximation method that is fairly quick and works on borderline cases. It is called the *method of successive approximations*.

Begin by assuming x is negligible as we have in the past. We then find $x = 2.3 \text{ x } 10^{-4}$. This value is indeed significant because subtracting it from 0.0030 changes that value. Now substitute x back into the final equation above in the *denominator only* and solve for the x in the numerator.

$$1.8 \text{ x } 10^{-5} = \frac{x^2}{0.0030 \text{ - } 0.000232}$$

$x = 2.2 \text{ x } 10^{-4}$

Since this value is virtually unchanged from the past value, we can accept it as accurate. This method will work conveniently to about $[HOAc]_i > 10K_a$. If the value of x is significantly different simply repeat until it doesn't change.

$pH = -\log(2.2 \times 10^{-4}) = 3.66$

$\% \text{ dissociation} = \dfrac{2.2 \times 10^{-4}M}{0.0030\ M} \times 100\% = 7.3\ \%$

Two things are noteworthy from this set of calculations. First, on going from 0.003 M to 3.0 M, we see two trends. Not surprisingly, the first is that increases in acid concentration leads to decreasing pH. There is something worth commenting on here, however. A thousand-fold increase in acetic acid concentration only decreases pH from 3.66 to 2.13 (the same change in strong acid concentration would cause a change of 3.00 units). In general, changes in weak acid concentration result in small changes in pH. Second, percent dissociation <u>decreases</u> dramatically in the same concentration range (from 7.3% to 0.24%). Thus, in dilute solution, a larger fraction of acid molecules ionize than in more concentrated solutions.

<u>Weak Bases</u>

Weak bases work much like weak acids, but there is a subtle difference. One thing to remember is that you must treat the reaction of the weak base with water (a <u>hydrolysis</u> reaction) just like you would a comparable reaction of a weak acid with water. A generic weak base reacts with water as follows:

$B + H_2O \rightleftharpoons HB^+ + OH^- \qquad\qquad K_b = \dfrac{[HB^+][OH^-]}{[B]}$
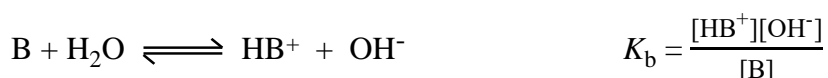
K_b is the <u>base dissociation constant</u>. Stronger bases have larger K_bs. Many uncharged, weak bases are similar to ammonia. These are bases with the generic formula NR_3. Where R can be any combination of hydrogen and groups binding to N through a carbon atom. Examples of such groups

include CH_3 (methyl), CH_2CH_3 (ethyl), C_6H_5 (phenyl) [for the methyl group the possible weak bases

are CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$). The other major class of weak bases are salts of conjugate

bases of weak acids. Sodium acetate and sodium bicarbonate (sodium hydrogen carbonate) are two

examples of such salts.

Ex. What is the pH of a 0.10 M NH_3 solution?

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
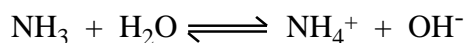
$$K_b = 1.8 \text{ x } 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$[NH_3]_i = 0.10\ M$ $[NH_3]_e = 0.10 - x\ M$

$[NH_4^+]_e = 0\ M$ $[NH_4^+]_e = [OH^-]e = x\ M$

$$\frac{x^2}{0.10 - x} = 1.8 \text{ x } 10^{-5}$$ just as for acids, assume $x \ll 0.10$

$$\frac{x^2}{0.10} = 1.8 \text{ x } 10^{-5}$$

$x = 1.34 \text{ x } 10^{-3}$ the assumption is valid

$[OH^-] = 1.34 \text{ x } 10^{-3}\ M \implies pOH = -\log(1.34 \text{ x } 10^{-3}) = 2.87$
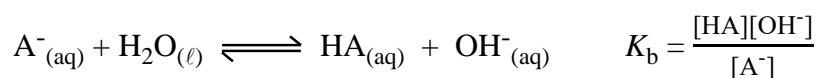
pH $= 14.00 - 2.87 = 11.13$

The Relationship between K_a and K_b

Let's briefly review some of what we've covered in this chapter. The conjugate base of a weak

acid is itself a weak base. When dissolved in water, this weak (conjugate) base abstracts a proton

from water to yield the original weak acid and hydroxide ion. Most weak bases are compounds of

this type. At first it might look awkward that the solution is basic since the weak acid is present, but

acidity is measured in terms of free H^+, not undissociated acid. The strength of a weak base formed

from a weak acid, depends on how strong the acid was in the first place. Consider two acids **HA**

and **HB**, where **HA** is the stronger of the two acids. Which will have the stronger conjugate base?

Our discussion of conjugate acid/base pairs told us that **B⁻** will be the stronger of the two, but what is the chemical justification? The strength of an acid depends on how easy it forms H⁺ ions. In this case, it happens more readily for HA. The strength of a weak base depends on the reverse process, that is, formation of a bond between the base and hydrogen. Since the breakup of HA occurs more readily, its formation cannot also be preferred. Thus, B⁻ is the stronger conjugate base.

The derivation of the mathematical relationship between K_a and K_b follows.

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \qquad\qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$A^-_{(aq)} + H_2O_{(\ell)} \rightleftharpoons HA_{(aq)} + OH^-_{(aq)} \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$$
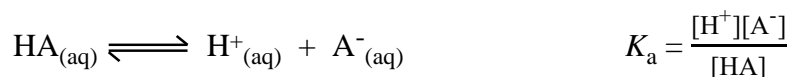
Notice that A⁻ and HA both appear on the right side of one equation and the left side of the other. Now when we add the two equations, we find something interesting occurs:

$$HA_{(aq)} + A^-_{(aq)} + H_2O_{(\ell)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} + HA_{(aq)} + OH^-_{(aq)}$$
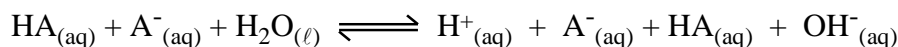
which simplifies to

$$H_2O_{(\ell)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \qquad K_w = [H^+][OH^-]$$

So how are the equilibrium constants related?

$$K_a K_b = \left(\frac{[H^+][\cancel{A^-}]}{\cancel{[HA]}}\right)\left(\frac{\cancel{[HA]}[OH^-]}{\cancel{[A^-]}}\right) = [H^+][OH^-] = K_w$$

The relationship $K_a K_b = K_w$ is necessary to determine the pH of a solution of a weak base formed from the conjugate base of a weak acid.

Ex. What is the pH of a 0.10 M sodium acetate solution?

K_b for NaOAc is not listed in Table 16.4 so it must be calculated.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$K_b = 5.6 \times 10^{-10} = \frac{[\text{HOAc}][\text{OH}^-]}{[\text{OAc}^-]} = \frac{x^2}{0.10 - x}$$

Assume x is negligible since $0.10 \gg K_b$

$$\frac{x^2}{0.10} = 5.6 \times 10^{-10}$$

$$x = 7.4 \times 10^{-6}$$

$$[\text{OH}^-] = 7.4 \times 10^{-6}\, M \Rightarrow \text{pOH} = -\log(7.4 \times 10^{-6}) = 5.13$$

$$\text{pH} = 14.00 - 5.13 = 9.87$$

Effect of Molecular Structure on Acid-Base Strength

One final question needs to be considered and answered regarding Brønsted-Lowry acids and bases: What factors control acid/base strengths and why do they do so? On several occasions we've touched on this, now we tackle it in depth. Last semester, a large portion of the class was devoted to chemical structure and the electronic nature of atoms and their interaction with neighboring atoms. What 3 major factors account for whether a substance is an acid or base, and how readily that substance will ionize?

Consider the generic acid HX, where X^- is any common anion. The more polar the H-X bond, the stronger will be the acid. Why? The products of dissolving an acid in water are the hydrogen ion and X^-. A very electronegative X atom or group will draw more electron density towards itself than will a less electronegative atom or group. In doing so, The H will begin to more closely approximate the final H^+ product, and the X will begin to resemble X^-. Since the starting acid more closely resembles the products with more electronegative groups, it takes less energy to separate the

molecule into ions. This results in a stronger acid.

Yet this can't be the only factor operating because HF is a weak acid, while HCl is a strong acid even though fluorine is more electronegative than chlorine. HF is also much weaker than HBr and HI, which are strong acids. The reason for this is the H-F bond is much stronger than the H-Cl, H-Br, or H-I bonds. The strong bond more than compensates for the bond polarity and holds the molecule largely intact when dissolved in water. This also accounts for why water ionizes only very slightly ($\sim 10^{-7}$ M) at room temperature even though the O-H bond is more polar than the H-Cl bond. (Thought question: If water ionized to a greater extent, would it be more acidic? Explain.) Down a group, binary acids become stronger because bond strengths weaken more rapidly than bond polarity decreases. Along a row, bond strengths change slowly so bond polarity is more important.

Finally, the stability of the conjugate base matters. The more stable the conjugate base, the more likely it is to be formed. Of the three factors, this is the one that is most difficult for you to predict and we won't discuss it further in this class.

What would happen if X, instead of being very electronegative, were very electropositive (very small electronegativity)? Bond polarity would reverse and electron density would be forced onto the hydrogen instead of pulled off it. The result is a series of complexes called binary metal hydrides (MH). These complexes are frequently bases, some being quite strong.

$$2 \text{ NaH}_{(s)} + \text{H}_2\text{O}_{(\ell)} \rightarrow 2 \text{ NaOH}_{(aq)} + \text{H}_{2 \, (g)}$$
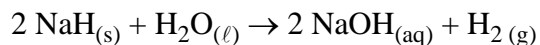
Oxyacids

The other major class of acids are those in which the hydrogen atom is attached to an oxygen that is part of a complex anion (e.g. $\text{HONO}_2 = \text{HNO}_3$). In these acids, the bond strength factor should not play a significant role. Why not? Because the hydrogen is always attached to an oxygen atom, and while small differences in bond strengths might exist, large ones should not. The result

is an acid whose strength depends almost solely on bond polarity. Apparently small changes in an

acid can change it from weak to strong. For example, H_2SO_3 and HNO_2 are weak acids, while

H_2SO_4 and HNO_3 are strong. Two factors can influence O-H bond polarity.

1) For acids with the same structure, acid strength increases with increasing electronegativity of the

    anion's central atom. For example, the HXO_4 series:

    $HOClO_2 > HOBrO_2 > HOIO_2$

2) For anions with the same central atom, increasing the oxidation number of that atom increases

    acid strength.

    $HOClO_3 > HOClO_2 > HOClO > HOCl$
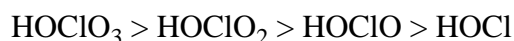
In both cases, acid strength increases because the change results in electron density being pulled

away from the oxygen to which the acidic hydrogen is bound. What happens when the central atom

is very electropositive? To answer this question, it is useful to imagine an example. What might

one be? While not a molecular compound, sodium hydroxide illustrates this idea nicely. Instead of

pulling electron density towards itself, the sodium pushes it onto the oxygen. The high

electronegativity of oxygen allows it to accept the electron density and ionization occurs between

the Na and O instead of in the O-H bond.

14.4 <u>Hydrolysis of Salts</u>

We have just seen that the salts of weak acids are weak bases (e.g. NaF, NaOAc, etc.). As

you've probably guessed, the reverse situation occurs as well. The conjugate acid of a weak base is

weakly acidic. The ammonium ion NH_4^+ is such a weak acid. An interesting difference between

the acidic and basic salts we've discussed until now is the nature of their acidity and basicity. All

of the acids you've seen react by releasing a proton into water. In contrast, while strong bases

directly release hydroxide ions into water, all weak bases react with water by abstracting a proton and releasing a proton. In general, reactions that break water up into H^+ and OH^- ions are called hydrolysis reactions.

A question that follows from this discussion is "Is it possible for such a reaction to result in an acidic solution?" The answer is yes. When most metal ions are dissolved in water, the solution becomes acidic. The attending hydrolysis reaction is shown below.

$$M^{n+} + H_2O \rightleftharpoons MOH^{(n-1)+} + H^+$$
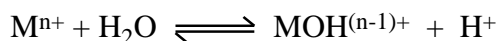
We'll discuss this reaction in more detail in Section 15.2. All cations, except the alkali metal ions and Ca^{2+}, Sr^{2+}, and Ba^{2+}, yield acidic aqueous solutions. In fact, these solutions can be fairly acidic; e.g. Al^{3+} solutions can be as acidic as acetic acid solutions.

Whether a solution is acidic or basic can be determined using the following guidelines.

a) Salts made from the reaction of a strong base with a strong acid (e.g. NaOH + HCl) yield neutral salts. Neither ion (Na^+ or Cl^-) hydrolyses water.

b) Salts made from a strong base and a weak acid (e.g. NaOH + HOAc). The salt will produce basic solutions because the base cation (Na^+) doesn't hydrolyze water, while the acid anion (OAc^-) does.

c) Salts made from a weak base and a strong acid (e.g. NH_3 + HCl). The salt will produce acidic solutions because the base cation (NH_4^+) releases H^+ ions, while the acid anion (OAc^-) doesn't hydrolyze water.

d) Salts made from the reaction of a weak base with a weak acid. In this case, both counterions will hydrolyze. If the weak acid is a stronger acid than the weak base is a base ($K_a > K_b$), the solution will be acidic. The converse is also true. Note, for these compounds one can usually expect even fairly concentrated solutions to have pHs not far from 7.

14.5 Polyprotic Acids

These are acids capable of donating more than one proton. For example, a <u>diprotic acid</u> donates

two protons. Each successive dissociation is designated K_{a1}, K_{a2}, …, with each constant usually

10^4-10^6 times smaller than the previous one. This is reasonable since it should be more difficult to

separate a proton from an anion than from a neutral molecule. As long as a K_a is at least a factor of

1000 from the next K_a, the other K_as can be ignored when doing calculations. An expanded version

of Example 19 (p. 794) illustrates this nicely.

Example 13: What are the concentrations of H_2CO_3, HCO_3^-, CO_3^{2-}, and H^+ in a solution that is

initially 0.0033 M in H_2CO_3? K_{a1} = 4.3 x 10^{-7}, K_{a2} = 4.7 x 10^{-11}

$$H_2CO_{3\ (aq)} \rightleftharpoons H^+_{\ (aq)} + HCO_{3\ (aq)}^- \qquad K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$4.3 \text{ x } 10^{-7} = \frac{x^2}{0.0033 - x} \quad \text{assume x} \ll 0.0033$$

$$4.3 \text{ x } 10^{-7} = \frac{x^2}{0.0033}$$

$$x = 1.2 \text{ x } 10^{-4} \qquad 1.2 \text{ x } 10^{-4} \ll 0.0033 \text{ so the assumption is valid}$$

Thus $[H_2CO_3]$ = 3.2 x 10^{-3} M \qquad and \qquad $[H^+]$ = $[HCO_3^-]$ = 1.2 x 10^{-4} M

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

$$4.7 \text{ x } 10^{-11} = \frac{(1.2 \text{ x } 10^{-4} + x)x}{1.2 \text{ x } 10^{-4} - x} \qquad \text{assume x} \ll 1.2 \text{ x } 10^{-4}$$

$$4.7 \text{ x } 10^{-11} = \frac{(1.2 \text{ x } 10^{-4})x}{1.2 \text{ x } 10^{-4}}$$

$$x = 4.7 \text{ x } 10^{-11} \qquad 4.7 \text{ x } 10^{-11} \ll 4.5 \text{ x } 10^{-5} \text{ so the assumption is valid}$$

Finally: $[CO_3^{2-}] = 4.7 \times 10^{-11}$. (The 5.6×10^{-11} in the summary is a mistake.)

This brings us to an important shortcut. When a polyprotic acid is dissolved in water, the concentration of the second and subsequent deprotonation products equals the corresponding K_a. For example: For H_3A: $[HA^{2-}] = K_{a2}$ and $[A^{3-}] = K_{a3}$.

14.6 Buffers

Solutions that resist a change in pH are called buffers. These solutions contain both a weak acid (to consume OH^-) and a weak base (to consume H^+). Most commonly they are a conjugate acid/base pair (e.g. acetic acid/sodium acetate). They undergo small pH changes when small amounts of strong acid or base are added.

To understand how a buffer works, consider one with equal parts weak acid and weak base, say 1.0 *M* HOAc and 1.0 *M* NaOAc. We know from earlier in the chapter increasing the concentration of a weak acid solution lowers the pH, but slowly. Increasing the concentration of a weak base solution increases the pH, but, again, slowly. Now, let's return to our buffer solution. If you add a little $NaOH_{(s)}$ to the buffer, you convert some of the HOAc to NaOAc. Thus, the concentration of acetic acid drops a small amount and the concentration of acetate ion increases a small amount. Both have the effect of increasing the pH a little, but if you had added the NaOH to pure water, the pH would have increased a lot more because all of the OH^- ions would have been left in solution. Buffers reduce pH changes until most of one of the components is used up.

It turns out the math is a little simpler for buffered solutions than for weak acids or bases dissolved in water. Because significant amounts of both an acid and its conjugate base are present, ionization is suppressed. Again, let's use acetic acid/sodium acetate as an example.

$$HOAc \rightleftharpoons H^+ + OAc^-$$
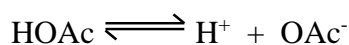
In the case of pure acetic acid: $[HOAc]_e = [HOAc]_i - x$,

$[H^+]_e = [OAc^-]_e = x$

In contrast, in a buffer the concentrations look like this: $[HOAc]_e = [HOAc]_i + x$

$[OAc^-]_e = [OAc^-]_i - x$

$[H^+]_e = x$

But according to Le Châtelier's principle, the addition of OAc⁻ retards the ionization of HOAc. This

results in an x that can be neglected in both its subtraction from $[HOAc]_i$ and addition to $[OAc^-]_i$.

The result is $[HOAc]_e = [HOAc]_i$ and $[OAc^-]_e = [OAc^-]_i$ for a buffer solution.

Consider the hypothetical acid HA: $HA \rightleftharpoons H^+ + A^-$ $K_a = \dfrac{[H^+][A^-]}{[HA]}$

and assume there is an appreciable amount of both HA and A⁻ present in solution so we can neglect

ionization.

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

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

now take the negative logarithm of each side:

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

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

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

In general: $pH = pK_a + \log\dfrac{[base]}{[acid]}$

This is called the Henderson-Hasselbach equation. It is very convenient if one works a lot of buffer

problems, although it isn't necessary. One may still work the problem as for a weak acid and I'll

work it both ways in the next example. For a pH change of 1 unit, 90% of the original weak acid or base must be consumed. (Prove this to yourself.)

One common mistake using the equation is forgetting which goes in the numerator, the acid or the base. Here's a simple way to remember: Adding a base increases pH and pH will only increase if the base goes in the numerator.

Addition of Strong Acids or Bases to Buffers

It is probably best to address this subject through an example, so we'll go over one here.

Ex: A buffer solution is made containing 0.50 moles of acetic acid and 0.50 moles of sodium acetate. The volume totals 1.0 L. What is it's pH? After adding 0.10 moles of hydroxide ion? 0.40 moles of hydroxide ion (total)?

Short method   Long method

$[HOAc]_i = \dfrac{0.50 \ mol_{HOAc}}{L} = 0.50 \ M$

$[OAc^-]_i = \dfrac{0.50 \ mol_{OAc-}}{L} = 0.50 \ M$

$pK_a = -\log (1.8 \times 10^{-5}) = 4.74$

a) $pH = 4.74 + \log\dfrac{0.50 \ M_{OAc-}}{0.50 \ M_{HOAc}} = 4.74$

b) $mol_{HOAc} = 0.50 \ mol_{HOAc} - 0.10 \ mol_{OH-}$ The calculation of the initial concentrations is

$= 0.40 \ mol$ same as for the first column.

$[HOAc] = \dfrac{0.40 \ mol_{HOAc}}{L} = 0.40 \ M$ $[HOAc]_e = 0.40 - x \ M$ $[H^+]_e = x \ M$

$mol_{OAc-} = 0.50 \ mol_{HOAc} + 0.10 \ mol_{OH-}$ $[OAc^-]_e = 0.60 + x \ M$

$= 0.60 \ mol$ $1.8 \times 10^{-5} = \dfrac{(x)(0.60 + x)}{(0.40 - x)}$

$$[\text{HOAc}] \;=\; \frac{0.60 \; \text{mol}_{\text{HOAc}}}{L} = 0.60 \; M \qquad\qquad \text{Since } [\text{HOAc}]_i > 100 K_a, \text{ assume } 0.40 - x \approx 0.40$$

$$pH = 4.74 + \log\frac{0.60 \; M_{\text{OAc-}}}{0.40 \; M_{\text{HOAc}}} = 4.92 \qquad\qquad \text{and } 0.60 + x = 0.60.$$

$$1.8 \times 10^{-5} = \frac{(x)(0.60)}{(0.40)}$$

$$x = [\text{H}^+] = 1.2 \times 10^{-5} \; M \;\; (\text{Check if assumption ok})$$

$$pH = -\log(1.2 \times 10^{-5}) = 4.92$$

If no buffer had been present (i.e. pure water), the pH would have been 13.00.

c)   This is worked the same as (b). The final pH is 5.69 (80% of the original acid is consumed here.)

The capacity of a buffer is the amount of strong acid or base that can be added without a significant change in pH. This definition may sound nebulous because what constitutes "significant change" depends on the situation. For example, if blood pH changes only ±0.05 pH units (see https://www.medicalnewstoday.com/articles/ph-of-blood) from its expected value (7.40) a medical condition will develop. A change of 0.5 units usually results in death. In more typical chemical reactions, maintaining a pH range of 0.1 pH units is typically unnecessary, so "significant" carries a different meaning. What is always true is that the more buffering agent present in solution, the higher the buffer capacity. Thus, 1 L of a buffer solution that is 1.0 M in both weak acid and weak base will have more capacity than 1 L of a buffer solution that is 0.1 M in both acid and base.

14.7   Acid-Base Titrations

You should review the section on titrations at the end of Chapter 4 (p. 208) before going on. You will be doing several titrations in CHM 218 and you need to be familiar with the theory and calculations before going into the laboratory.

Recall that a titration is an experiment in which a solution of known concentration is reacted with a known volume of a solution of unknown concentration in order to measure the latter's concentration. Historically, the end of reaction was signified with an organic dye that changed color when the reaction was complete. Today, pH meters allow the endpoints to be determined with greater precision.

Strong Acid-Strong Base Titrations

Consider the titration of a known concentration of the strong base NaOH (e.g. 0.10 M) into a solution of an unknown concentration of the strong acid HCl. The most convenient method of following a titration is to make a plot of the volume of added titrant $vs.$ pH. Initially, the pH of the initial acid solution is quite low (for a 0.10 M HCl solution, pH = 1.00). The pH will increase slowly at the beginning. When the number of added moles of base begins to approach the number of moles of acid in the unknown solution the rate of pH increase will accelerate. Typically, within a few tenths of a milliliter of the equivalence point pH will change several units. (The equivalence point occurs when the moles of titrant equal the moles of unknown.) The pH will continue to increase rapidly for a short distance before beginning to level off below the pH of the base solution (remember it is diluted by the water in the acid solution so the final solution will never achieve a pH of 13.00). This experiment is shown graphically below.
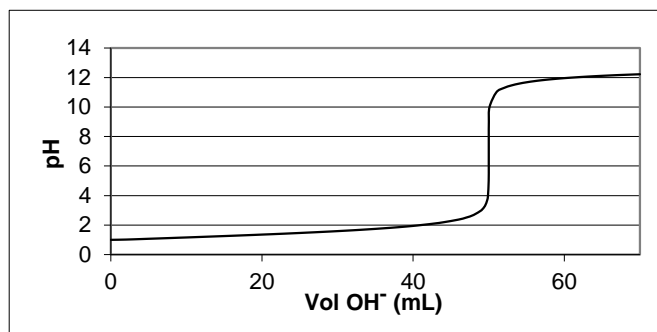
Before going further, here's a question to think about: How do we know when the equivalence

point occurs? In real life, we don't calculate the curve, an experiment is performed in which we measure pH as a function of added acid or base. Today we use a pH meter, but that wasn't available a hundred years ago. Before pH meters (and even today when only the endpoint is needed) organic dyes (indicators) were used to signal when the titration was complete. These dyes dramatically changed color on going from a protonated to deprotonated form. For example, phenolphthalein changes from colorless ($C_{20}H_{14}O_3$) to bright pink ($C_{20}H_{13}O_3^-$) at a pH of 8.2 – 10. It is interesting to note that phenolphthalein is used to determine the endpoints of strong acid and base titrations even though their endpoints occur at pH = 7. Here are two questions for you: (1) Why is it all right to use phenolphthalein here? and (2) One hundred years ago, how did they know to use phenolphthalein instead of methyl orange (pH change from 3.2 – 4.4 red = acid form, yellow = base form) for strong acid/base titrations? Find the answers below.

We should now calculate some of the points on the displayed titration curve (Figure 14.18, p. 807). The initial point is simply the pH of a 0.100 M hydrochloric acid solution. Let's look at the addition of 10 mL of 0.100 M sodium hydroxide solution and 49.9 mL. Try calculating the pH after adding 49.99 and 49.99 mL of the sodium hydroxide solution on your own.

We begin by determining the number of moles of acid in the original solution:

$$\text{mol}_{H+}(\text{initial}) = (0.0500 \text{ L}_{\text{soln}})\left(\frac{0.100 \text{ mol}_{HCl}}{\text{L}_{\text{soln}}}\right)\left(\frac{1 \text{ mol}_{H+}}{1 \text{ mol}_{HCl}}\right) = 0.00500 \text{ mol}_{H+}$$

Now write out the balanced equation and determine the number of moles of base added:

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O_{(\ell)} + NaCl_{(aq)}$$
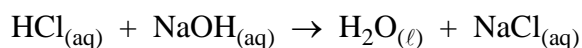
$$\text{mol}_{OH-} = (0.0100 \text{ L}_{\text{soln}})\left(\frac{0.100 \text{ mol}_{NaOH}}{\text{L}_{\text{soln}}}\right)\left(\frac{1 \text{ mol}_{OH-}}{1 \text{ mol}_{NaOH}}\right) = 0.00100 \text{ mol}_{OH-}$$

The amount of acid remaining in solution equals the difference between these numbers, then calculate concentration, and finally pH.

$$\text{mol}_{H+}(\text{end}) = 0.00500 \text{ mol}_{H+} - 0.00100 \text{ mol}_{OH-} = 0.00400 \text{ mol}_{H+}$$

$$[H^+] = \frac{0.00400 \text{ mol}_{H+}}{0.0600 \text{ L}_{soln}} = 0.0667 \ M$$

$$pH = -\log(0.0667) = 1.18$$

In an exactly analogous manner, the pH of the solution after adding 49.9 mL of sodium hydroxide solution is 4.00. It might strike you as really odd that the pH increases so dramatically on addition of such small amounts. After all, the first 10 mL of base increases pH by 0.18 units, but the 0.9 mL increase from 49.0 mL to 49.9 mL results in a 1.00 unit increase (see book for the 49 mL value). Remember the pH scale is logarithmic. As the titration approaches equivalence, $[H^+]$ approaches zero. Thus, very small amounts of base cause a large percentage change in remaining acid concentration.

Before answering the two questions raised on the previous page, we need to go over a definition. The <u>endpoint</u> of a titration is the volume of titrant which causes the indicator to change color. In principle, this can lead to a difference between the volume read at the endpoint and that required for the equivalence point. If you repeat the calculations above for 50.001 mL and 50.01 mL of added base, you'll see that it takes a negligibly small amount of base to trigger the indicator and so we can use the endpoint volume as the equivalence point volume. Phenolphthalein works because even though it doesn't change color until $pH \cong 8.5$, the titration curve is almost vertical here. Only a small fraction of a drop moves pH from 7 to 8.5. Methyl orange, on the other, hand will require several mL of titrant to effect a color change. One requirement for an indicator is that the color change occurs rapidly. They knew that the dyes worked because they could use authentic samples of an acid and its conjugate base to track color changes.

Weak Acid/Base-Strong Base/Acid Titrations

There are two significant differences between these titrations and those where both components

are strong. The first is the appearance of the curve. Because the acid or base being titrated is weak,

the vertical portion of the curve is compressed somewhat (see below). The second difference is that

the final pH is lower than 7.00 for a strong acid/weak base titration and higher than 7.00 for a strong

base/weak acid titration. This is because the products of a strong base/weak acid titration are water

and the conjugate base of the weak acid. Remember that this conjugate base will also be a weak

base. Remember, neutralizing the weak acid means completely removing its proton, not that the

solution has a neutral pH.   The calculations are more involved because one must determine the

equilibrium value each time. Fortunately, the Henderson-Hasselbach equation can be used for these

titrations.
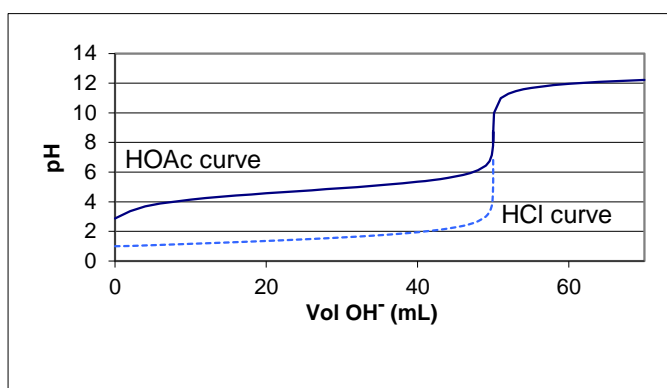
Finally, the weaker the acid or base, the less pronounced is the break in the titration curve until

at a K_a or K_b of much smaller than 10^{-7}, it becomes difficult to see where it occurs (see Figure 14.18,

p. 807). Everything said so far about weak acids applies in reverse to weak bases.

October 10, 2022