Faculty of Science

Unit 4:
Acids and Bases

CHEM 1523
Principles of Chemistry

Table Of Contents

Unit 4: Acids and Bases

Unit 4: Acids and Bases

Overview

From early times, man has classified various substances into three categories: acids, bases, and salts. The term **acid** is derived from the Latin *acidus*, meaning sour, or *acetum*, meaning vinegar. (The acid component of vinegar is acetic acid, CH_3COOH.) When grapes were first fermented to make wine, people learned that the wine became sour or vinegary if the fermentation process continued for too long. Substances classified as acids had the following common characteristics:

- Sour taste

- Could change the colour of certain dyes (e.g., blue litmus to red)

- Could react with certain metals (e.g., Mg, Zn) to produce hydrogen gas

- Could react with a base to produce a salt

Alkali, a word derived from the Arabic word for ashes, is an alternate term for **base**. In fact, for many centuries, the principal source of alkali was wood ashes. Alkalis or bases were considered to have the following common characteristics:

- Bitter taste

- Could change the colour of certain dyes (e.g., red litmus to blue)

- A slimy or soapy feeling

- Could react with an acid to produce a salt

Salts, formed from the neutralization reaction of acids and bases, were also widely known in early times. Examples are sodium chloride (NaCl), ammonium nitrate (NH_4NO_3), and copper(II) sulphate ($CuSO_4$). The naming of salts was covered in CHEM 1503.

This unit introduces the newer definitions of acids and bases. These definitions developed as a result of a growing understanding of ions in solution (Arrhenius definition) and were later extended (by Brønsted) to fit non-aqueous solutions. Eventually, the much broader Lewis definitions were based on the behaviour of electron pairs. Also covered in this unit is acid or base strength and its relationship to chemical structure. However, most of this unit concentrates on the application of equilibrium principles, covered in the last unit, to solutions of acids, bases, and salts. These calculations have an important practical application in many areas of chemistry. Since this unit deals mainly with calculations, you may lose sight of the fact that acids and bases are real chemicals involved in real everyday use.
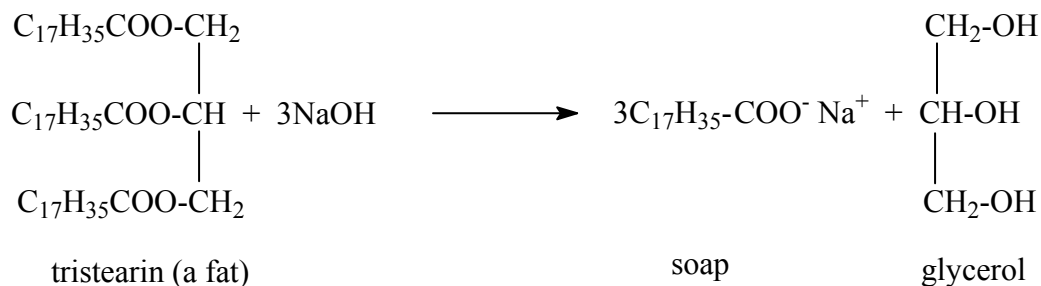
In this introductory section, we look at a few of the uses of some of the more common acids and bases. As you work through the remainder of the unit, remember that the calculations you are being shown could be needed in any of the following industrial or medical applications.

Hydrochloric acid (HCl) is often known by its commercial name of *muriatic acid* and, in concentrated form, it is used to clean bricks, metal, and cement. HCl is also produced in the stomach, where it aids in the digestion of protein. The major use of **nitric acid (HNO$_3$)** is in the production of fertilizers, dyes, plastics, and explosives. It is also used as a test for albumin in the urine because of its ability to coagulate protein. **Sulphuric acid (H$_2$SO$_4$)** is used mainly to produce explosives, fertilizers, dyes, paper, and glue. It is the acid used in lead storage (car) batteries and is thus sometimes called *battery acid*. **Phosphoric acid (H$_3$PO$_4$)** is used in numerous ways: fertilizers, flavourings in soft drinks, dental cement for false teeth. **Boric acid (H$_3$BO$_3$)** is used as an antiseptic, germicide, and eyewash. Misuse, however, can lead to boric acid poisoning. A lethal dose varies from 5 to 20 g of boric acid and can be absorbed through the skin.

You should, of course, *never test any chemical for taste*. Take the word of chemistry books and your knowledge of foods that acids are sour and bases are bitter.

The above-mentioned acids are all **mineral acids** as opposed to **organic acids**. Organic compounds used to be considered as coming from living things, but nowadays the definition of organic is those compounds containing carbon and hydrogen, and usually oxygen, nitrogen, sulphur, phosphorus, or halogens. Organic molecules with acidic properties are considered to be organic acids. Examples of organic acids that are derived from living things are acetic acid (from fermented fruits), citric acid (found in citrus fruit), and ascorbic acid (vitamin C).

Bases have important industrial uses. **Sodium hydroxide (NaOH),** known commercially as *lye*, is used in drain cleaners, and to make soap and cellophane. An example of soap making is as follows:

$$C_{17}H_{35}COO\text{-}CH_2$$
$$|$$
$$C_{17}H_{35}COO\text{-}CH + 3NaOH \longrightarrow 3C_{17}H_{35}\text{-}COO^-\ Na^+ + CH\text{-}OH$$
$$|$$
$$C_{17}H_{35}COO\text{-}CH_2$$

$$CH_2\text{-}OH$$
$$|$$
$$CH_2\text{-}OH$$

tristearin (a fat)   soap   glycerol

To make soap, fat or oil is reacted with lye (NaOH). The mixture is heated, giving soap and glycerol. **Calcium hydroxide [Ca(OH)$_2$],** in solution known as *lime-water*, is used in the construction industry in mortar, plaster, and cement.

It is also used medically as an antacid. **Ammonia (NH₃)** is used as a household cleaner and is an ingredient in smelling salts. Industrially, its uses include fertilizers, plastics, and textile manufacture. **Magnesium hydroxide [Mg(OH)₂]** is known medicinally as *milk of magnesia*. It is used in small doses as an antacid and in larger doses as a laxative. Biological fluids are generally strongly buffered. The pH range (acid or base range) for physiological reactions must be very closely controlled, usually over fairly narrow limits. The pH of human blood is buffered to remain in the range of 7.35 to 7.44. Should the pH fall outside these limits for any reason, the blood loses its ability to transport oxygen from the lungs to the body cells. The lymphatic and spinal fluids are also buffered. This unit describes buffer calculations and applications. If you do further courses in chemistry, biochemistry, or physiology, these general buffer principles will be applicable.

Learning Outcomes

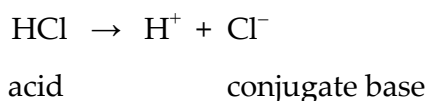Once you are finished this unit, you should be able to:

- Define acids and bases using the Arrhenius, Brønsted, and Lewis theories.

- Write acid-base conjugate pairs for given compounds.

- Explain the relationship between structure and acid-base strength.

- Write equations and equilibrium expressions for aqueous solutions of acids and bases.

- Express [H$^+$] as pH, pOH, or [OH$^-$], and vice versa.

- Distinguish between weak and strong for acids and bases.

- Calculate the pH of solutions of weak acids or bases, or strong acids or bases, including polyprotic acids and bases.

- Explain why solutions of certain salts are acidic or basic and calculate the pH of solutions of such salts.

- Calculate the pH of buffer solutions, pH changes in buffer solutions, and methods of preparing buffers.

- Perform calculations relating solubility and pH.

- Construct pH titration curves.

- Explain the theory of acid-base indicators and their use.

Definitions

Review Section 4.3 and study Section 15.1 in your textbook. You should know the Arrhenius definitions of acids and bases, which depend on the fact that in an aqueous solution an Arrhenius acid gives rise to protons and an Arrhenius base to hydroxide ions. These definitions were not "wrong," but they were not general enough. The Arrhenius definition implied that the OH^- ion came from within the base. This is true for NaOH but not for bases such as NH_3. A more general definition is given by the Brønsted theory, which states that an acid is defined as being a proton donor and a base as a proton acceptor. This idea of **proton transfer** is a more general and thus more acceptable concept. You should also know what is meant by conjugate acids and conjugate bases. A conjugate base is what you have left after a proton is removed. A conjugate acid is what you form when a proton is added. The following problems illustrate conjugate acid–base pairs for some common neutral and charged species.

Problem: Indicate the conjugate base for each of the following Brønsted acids: HCl, H_2SO_4, HSO_4^-, and NH_4^+.

Solution:

$$HCl \;\rightarrow\; H^+ + Cl^-$$
$$\text{acid} \qquad\qquad \text{conjugate base}$$

The conjugate acid-base pair here is HCl/Cl^-.

$$H_2SO_4 \;\rightarrow\; H^+ + HSO_4^-$$
$$\text{acid} \qquad\quad \text{conjugate base}$$
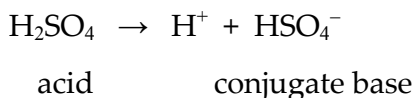
The conjugate acid-base pair here is H_2SO_4/HSO_4^-.

$$HSO_4^- \;\rightarrow\; H^+ + SO_4^{2-}$$
$$\text{acid} \qquad\qquad \text{conjugate base}$$
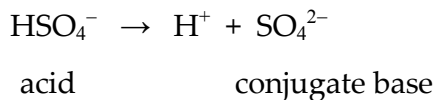
The conjugate acid-base pair here is HSO_4^-/SO_4^{2-}.

$$NH_4^+ \;\rightarrow\; H^+ + NH_3$$
$$\text{acid} \qquad\qquad \text{conjugate base}$$
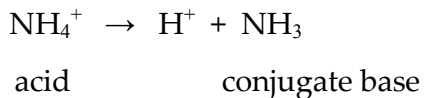
The conjugate acid-base pair here is NH_4^+/NH_3.

Problem: Indicate the conjugate base for each of the following Brønsted bases: NH_3, OH^-, and $Mg(OH)^+$.

Solution:

$$NH_3 + H^+ \rightarrow NH_4^+$$

base   conjugate acid
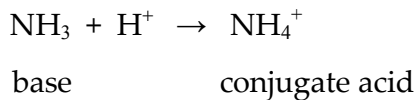
The conjugate base-acid pair here is NH_3/NH_4^+.

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

base   conjugate acid

The conjugate base-acid pair here is OH^-/H_2O.

$$Mg(OH)^+ + H^+ \rightarrow Mg(OH_2)^{2+}$$

base   conjugate acid
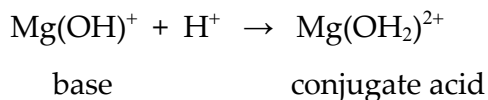
The conjugate base-acid pair here is $Mg(OH)^+/Mg(OH_2)^{2+}$.

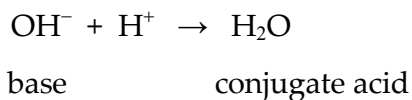But protons do not exist as independent species. A bare proton, represented by H^+, contains such a high density of electric charge, due to its minute volume, that it can have no independent existence. It is always attached to something, usually a water molecule. If there is another species that can hold the H^+ at a lower free energy (i.e., a stronger base), then the proton will be transferred. To be a proton acceptor, it must have something to accept the H^+ from. Similarly, to be a proton donor, an acid must have something to donate that proton to. This involves a second acid-base conjugate pair. Usually this second pair is the solvent. Some further examples of acid-base conjugate pairs are shown below. This time the solvent is shown acting as the second acid-base conjugate pair.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

acid 1   base 2   acid 2   base 1
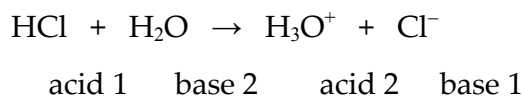
Acid 1 has as its conjugate base the species labeled base 1.

Base 2 has as its conjugate acid the species labeled acid 2.

Substances such as water that can accept or donate an H^+ are termed **amphoteric**. Other examples of amphoteric species are HSO_4^-, HCO_3^-, and NH_3. Table 15.2 in your textbook lists a number of acid-base conjugate pairs.

Work through Example 15.1 and its practice exercise from your textbook.

Autoionization of Water and the pH Scale

Study Sections 15.2 and 15.3 of your textbook.

Although protons do not exist as "H^+", it is not unusual to represent them in this way. Some textbooks use the hydronium ion form, H_3O^+, although most evidence points to a hydrated $H_9O_4^+$ species. Here, we use the same notation as your textbook, H^+, to represent any hydrated form of a proton. The **autoprotolysis** of water

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

or

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
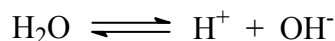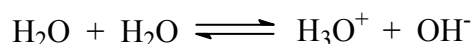
gives an equilibrium expression involving only $[H^+]$, $[OH^-]$, and $[H_2O]$. Since the concentration of H_2O is constant, this gives rise to the **ion product of water**,

$K_w = [H^+][OH^-] = 10^{-14}$, at 25ºC. In any aqueous solution at 25ºC, the product

$[H^+] \times [OH^-]$ always equals 10^{-14}. (In this course you can assume that the aqueous solutions you are dealing with are at 25ºC or at a temperature where the K_w value is extremely close to 10^{-14}.) If the $[H^+]$ is greater than 10^{-7}, then the $[OH^-]$ is less than 10^{-7}. A solution with $[H^+]$ greater than 10^{-7} is acidic. If the $[OH^-]$ is greater than 10^{-7}, the solution is basic. Go over Example 15.2 and its practice exercise in your textbook.

The symbol **p** is an important concept in this unit and this symbol is translated as the negative logarithm. pH is the negative logarithm of the $[H^+]$; pOH is the negative logarithm of $[OH^-]$; pK_a is the negative logarithm of K_a, pK_b is the negative logarithm of K_b; and pK_w is the negative logarithm of K_w. (The value of pK_w is 14.)

You have probably already heard of the acidity scale, **pH**. A few years ago the big "advance" in shampoo was *pH-balanced shampoo*. Table 15.1 in your textbook gives you pH values of some common materials. If you have ever tried your hand at wine making, you will know how important it is to maintain the right acidity balance and that wine-making kits usually come equipped with pH test kits. As well, swimming pool owners regularly check the pH of the pool water.

You must be able to convert $[H^+]$ or $[OH^-]$ to pH (or to pOH, although the pOH scale is not often used). You must also be able to convert a pH value to an $[H^+]$ or an $[OH^-]$ value. Work through Examples 15.3 to 15.5 and their practice exercises for practice on this. Scientific calculators make these calculations very straightforward and, on most of these calculators, the steps for obtaining the logarithm are:

enter value,

press ⬚log⬚ key,

press ⬚=⬚ key.   (optional)

The steps for the antilog are:

enter value

press ⬚INV⬚ key   (or ⬚2nd F⬚ key)

press ⬚log⬚ key

press ⬚=⬚ key   (optional)

Calculators do differ, so make sure you can use yours for these operations. If you do not have a scientific calculator or a calculator with these log and antilog functions, we recommend that you obtain one because it will save you a lot of time. Appendix 4 in your textbook gives a full account of logarithms. You may want to review this material before you attempt the following problems. The facts to remember here are:

$$pH = -\log[H^+]$$
$$pOH = -\log[OH^-]$$
$$[H^+][OH^-] = 10^{-14}$$
$$pH + pOH = 14$$

Problem: The $[H^+]$ of a solution is 4.5×10^{-4}. What is

    a.   The $[OH^-]$?
    b.   The pH?
    c.   The pOH of this solution?

Solution:

    a. $[OH^-] = 10^{-14} / [H^+]$

            $10^{-14} / (4.5 \times 10^{-4}) = 2.2. \times 10^{-11}$

    b. $pH = -\log[H^+] = -\log(4.5 \times 10^{-4}) = 3.35$

    c. $pOH = -\log[OH^-] = -\log(2.22 \times 10^{-11}) = 10.65$

        You can check here that pH + pOH does equal 14:

            $3.35 + 10.65 = 14.$

A note on significant figures: pH 3.35 has two significant figures since it is a log value and the 3 before the decimal point indicates the value of the exponent.

Problem: A basic solution has a pH of 12.20. Calculate:

a. The pOH

b. The $[H^+]$

c. The $[OH^-]$ of this solution

Solution:

a. pOH = 14 – pH = 14 – 12.20 = 1.80

b. $[H^+]$ = antilog (–pH) = antilog (–12.20) = 6.3×10^{-13}

c. $[OH^-]$ = antilog (–pOH) = antilog (–1.80) = 1.6×10^{-2}

   Check: $[H^+][OH^-] = 6.3 \times 10^{-13} \times 1.6 \times 10^{-2} = 10^{-14}$

Strength of Acids and Bases

Study Section 15.4 in your textbook. This is an important section, so be sure to go through it carefully and that you understand the following summary points.

The words *strong* and *weak* have specific meaning in acid-base chemistry. In this unit, we consider all acids that are stronger than H_3O^+ to be **strong acids**. This is the usual practice; which means that the strong acids are considered completely dissociated in water. The strong acids that you will normally encounter are HCl, HNO_3, $HClO_4$, and the first dissociation of H_2SO_4 (HBr and HI are also strong acids). In dilute aqueous solution, these acids are regarded as practically 100% dissociated. You could write their reaction with water as follows, using HCl as an example:

$$HCl \ + \ H_2O \ \rightarrow \ H_3O^+ \ + \ Cl^-$$
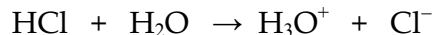
An equilibrium constant for this reaction would be very large—the equilibrium lies very much to the right. For these dilute aqueous solutions of weak acids, the dissociation is normally less than 1%. In reality, there is no firm dividing line between concentrated and dilute. In this unit, we consider solutions of 1 M or less to be dilute.

Note the following important points.

- The stronger the acid, the weaker its conjugate base (and vice versa).

- H_3O^+ is the strongest acid that can exist in aqueous solution.

- OH^- is the strongest base that can exist in aqueous solution.

Now work through Examples 15.6 and 15.7 in your textbook, and complete their practice exercises.

The Levelling Effect

Although the four acids HCl, HNO$_3$, HClO$_4$, and the first dissociation of H$_2$SO$_4$, are considered to be of the same strength in aqueous solution, they do dissociate to different degrees in solvents that are weaker bases than water. This is known as the **levelling effect**. You should understand that in other solvents there is a difference in the strengths of these strong acids. An appropriate analogy is that of a grown man having a tug-of-war against two boys: the man wins the competition, but you cannot determine from this outcome whether one boy is stronger than the other!

Figure 4.1 in this unit demonstrates the levelling effect. The diagram shows a number of acid-base species arranged in increasing order of acid strength. Any acid (shown on the left) can donate protons to any base (on the right) that is below it on the diagram. The greater the vertical distance separating acid and base, the more complete the reaction.

Note the position of H$_2$O in this diagram. Near the top, it appears as the conjugate base of H$_3$O$^+$. HClO$_4$, H$_2$SO$_4$, HCl, and HNO$_3$ are above the H$_3$O$^+$/H$_2$O system. They virtually completely donate their protons to the base H$_2$O. They are considered as being completely dissociated. In aqueous solution they act as equally strong acids despite their different free energy changes for proton transfer. This is the leveling effect.

Towards the bottom of the diagram, the H$_2$O/OH$^-$ pair marks the point where strong bases are "levelled." If you were to add some sodium oxide, Na$_2$O, or sodamide, NaNH$_2$, to water, you would get OH$^-$ ions from Na$_2$O, and OH$^-$ ions and ammonia from the sodamide. Oxide and amide ions are such strong bases that they will accept protons from water, giving the conjugate acids of the ions and leaving OH$^-$ from the water molecule. This can all be summarized by saying that *acids stronger than H$_3$O$^+$ and bases stronger than OH$^-$ cannot exist in aqueous solution*.

Acids		Bases
(proton sources)		(proton sinks)

$HClO_4$ ——— ClO_4^-

H_2SO_4 ——— HSO_4^-

HCl ——— Cl^-

Stronger acid ↑

HNO_3 ——— NO_3^-

H_3O^+ ——————— H_2O

HSO_4^- ——— SO_4^{2-}
$Fe(H_2O)_6^{3+}$ ——— $Fe(H_2O)_5OH^{2+}$

CH_3COOH ——— CH_3COO^-
$Al(H_2O)_6^{3+}$ ——— $Al(H_2O)_5OH^{2+}$
H_2CO_3 ——— HCO_3^-
HCN ——— CN^-
NH_4^+ ——— NH_3

C_6H_5OH ——— $C_6H_5O^-$
HCO_3^- ——— CO_3^{2-}

HPO_4^{2-} ——— PO_4^{3-}

H_2O ——————— OH^-

Stronger base ↓
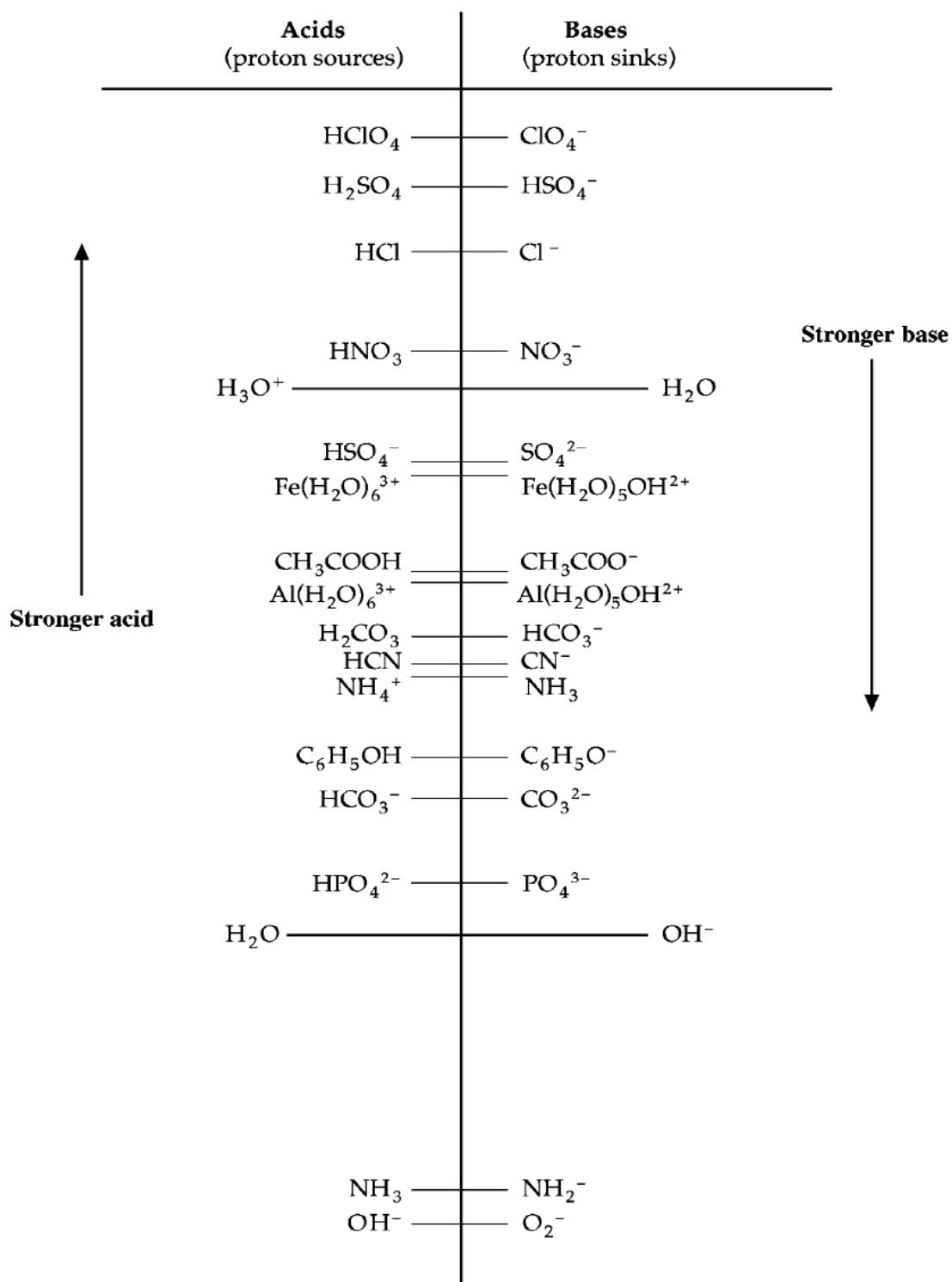
NH_3 ——— NH_2^-
OH^- ——— O_2^-

Figure 4.1: Comparative acid/base strengths.

Weak Acids and Weak Bases

Study Sections 15.5 and 15.6 in your textbook.

Students often ask, "How can I know if an acid is strong or weak?" There are a number of ways, but the easiest is to know (i.e., memorize) that the strong acids are HCl, HBr, HI, HNO_3, $HClO_4$, and the first dissociation of H_2SO_4. Any other acid you encounter is in all probability a **weak acid**. You can check this by K_a values. Weak acids have small K_a values (K_a values are rarely quoted for strong acids). All organic acids are weak. A non-scientific approach (but one that works 99.9% of the time) is to say that if you have never heard of the acid before, or if the name is unusual, then it is a weak acid. For example, you have probably never heard of the following acids: capronic acid, trimethylacetic acid, acetoacetic acid, succinic acid, mevalonic acid, and abietic acid. These are all organic acids and are all weak acids. Do not fall into the trap of assuming that just because a compound contains H in its formula, it is an acid. There are thousands (even millions) of compounds containing hydrogen that are not acids. In CHEM 1503, you studied some organic chemistry and found that organic compounds that are acids contain the word "acid" in their name and the functional group –COOH in their structure.

For a weak acid, the equilibrium lies very much to the left. The acid, although dissolved in water, is not dissociated. There is a big difference between the terms *dissolved* and *dissociated*. The process of **dissociation** is simply the unpairing and separation of ions. If the substance is an acid, the proton ion cannot, on dissociation, just float off. It must be donated to an acceptor such as water. The weak acid dissociation expression is

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

This is for the dissociation of the general weak acid HA.
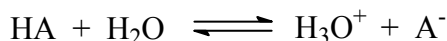
$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

The actual equilibrium expression for this includes the concentration of water:

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

However, water is the solvent and its very large concentration of around 55 M does not change in these dilute solutions. If the constant concentration of water is included with the constant value of K,

$$K \times [H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Then the total left-hand side of this expression is a constant: $K \times [H_2O]$ is known as K_a, the acid dissociation constant. This means that for the dissociation of a weak acid you do not include the H_2O term. It is already included in the K_a value.

You will find that all these principles that we have applied to acids can be applied to bases in an analogous manner. Bases stronger than OH^- are said to be strong bases since they are virtually 100% dissociated in water. K_b values apply to weak bases and include the value for the concentration of water. Again, you can tell if a substance is a weak base by whether it is not a simple metal hydroxide like NaOH, KOH, or $Ba(OH)_2$, or if it has an unusual name, or one you have not heard before. (With a few exceptions, strong bases are metal hydroxides.) Note that $Ca(OH)_2$ is virtually insoluble but what does dissolve is dissociated. $Ca(OH)_2$ is thus a strong base. Despite, or perhaps because of, its low solubility, it is widely used for treating soil and water. $Ca(OH)_2$ is being spread in lakes and forests to counter acid rain.

You do not need to memorize K_a and K_b values, since they will be given to you. Take a good look at Table 15.3 in your textbook. Note that for each weak acid (with a K_a value) there is listed its conjugate base (with a K_b value).

Work through Examples 15.8, 15.9, and 15.10 in your textbook, and their practice exercises. You should see that all these calculations are based on the same procedure that was followed in Unit 3 of this course to determine equilibrium concentrations. Your textbook goes through the procedure each time, but—provided you realize that you are simplifying and making assumptions—you can use the following formulas.

$$
\begin{array}{ll}
\text{For a weak acid} & [H^+] = \sqrt{K_a \times \text{acid conc.}} \\
\text{For a weak base} & [OH^-] = \sqrt{K_b \times \text{base conc.}}
\end{array}
$$

These formulas apply only as an approximation when the amount dissociated is very much less than the original concentration. It is never a good idea to use a formula without understanding where the formula comes from. If you choose to use this formula, you must be aware that it is only valid as far as the approximation is valid. Always check that your answer fits the 5% rule as explained in Unit 3. If it does not, you should set out the calculation as an equilibrium problem and solve using the quadratic formula. But K_a is usually small, so you can usually use these time-saving formulas.

Now work through the following problems.

Problem: Calculate the pH of a solution of 0.245 M HF.

Solution: HF is a weak acid with K_a of 7.2×10^{-4}. We find

$$[H^+] = \sqrt{K_a \text{ x acid conc.}}$$

$$= \sqrt{7.1 \text{ x } 10^{-4} \text{ x } 0.245}$$

$$= 1.3 \text{ x } 10^{-2}.$$

Check: 5% of 0.245 is 1.23×10^{-2}. The answer, 1.3×10^{-2}, is greater than this, so the approximation is *not* valid. You should now have to redo the calculation as a full equilibrium problem and solve the quadratic equation. Use this value of $[H^+]$ to find the pH of the solution.

Problem: Calculate the pH of a solution of 5.8 M NH_3.

Solution: We find

$$[OH^-] = \sqrt{K_b \times \text{base conc.}}$$

$$= \sqrt{1.8 \times 10^{-5} \times 5.8}$$

$$= 1.0 \times 10^{-2}.$$

Check: 5% of 5.8 is 2.9×10^{-1}, so the assumption is valid.

$$pOH = 2 - \log 1.0 = 2.00$$

$$pH = 14 - 2.00 = 12.00$$

Note that in this last example the answer is only approximate because the high solution concentration means ideal solution behaviour is not followed. An **ideal solution** is one where each molecule behaves as if it were surrounded entirely by molecules of like kind. The components of an ideal solution experience no modification other than that of dilution (see Unit 1 of CHEM 1503). The electrostatic attractions between oppositely charged ions mean that high-concentration solutions cannot be considered as ideal. These formulas can only be used for solutions of neutral (non-ionic) weak acids or weak bases. They cannot be used to determine $[H^+]$ for solutions of conjugate bases or conjugate acids.

Problem: Calculate the $[H^+]$ of a 0.020 M solution of hypochlorous acid. K_a for HClO is 3.2×10^{-8}.

Solution: Hypochlorous acid, HClO, is a weak acid. We find

$$[H^+] = \sqrt{K_a \times \text{acid conc.}}$$

$$= \sqrt{3.2 \times 10^{-8} \times 0.020}$$

$$= 2.5 \times 10^{-5}$$

Check: 5% of 0.020 M is 1.0×10^{-3} M, and $2.5 \times 10^{-5} < 1.0 \times 10^{-3}$, so the assumption is valid.

Problem: Calculate the pH of a 0.0050 M solution of codeine. Codeine is a weak base with K_b of 1.63×10^{-6}.

Solution: We find

$$[OH^-] = \sqrt{K_b \times \text{base conc.}}$$

$$= \sqrt{1.63 \times 10^{-6} \times 0.0050}$$

$$= 9.0 \times 10^{-5}$$

Check: 5% of 0.0050 is 2.5×10^{-4} and $9.0 \times 10^{-5} < 2.5 \times 10^{-4}$, so the assumption is valid.

$$pOH = 5 - \log 9.0 = 4.04$$

$$pH = 14 - 4.04 = 9.96$$

Per cent ionization (or per cent dissociation) is another way of expressing the strength of an acid (or a base). You often have to first calculate $[H^+]$ (or $[OH^-]$) in order to determine per cent ionization.

Relationship between Conjugate Acid-Base Ionization Constants

Study Section 15.7 of your textbook. Note the following about the reaction of a conjugate base, A^-, with water.

$$A^- + H_2O \rightleftharpoons HA + OH^-$$
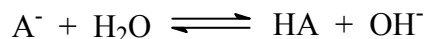
This is not the reverse of the ionization of the weak acid HA.

A conjugate acid of a weak base produces an acidic solution (and the conjugate base of a weak acid produces a basic solution).

Make sure you follow through the derivation of the relationship

$$K_a K_b = K_w$$

Polyprotic Acids and Bases

Study Section 15.8 of your textbook. You should be able to write the relevant equations and equilibrium expressions for the stepwise dissociations of polyprotic acids. Since the first dissociation, K_1, is always greater than those of subsequent dissociations, you can treat a polyprotic weak acid as a monoprotic species in order to estimate the pH of such a solution. (The contribution of protons from second or third dissociations is considered negligible except in the case of H_2SO_4, where the second ionization constant of 1.3×10^{-2} is fairly large.) Work through Example 15.11 in the textbook and its practice exercise. In this example, the H^+ concentration from the second dissociation is about 0.1% of the value from the first dissociation and can be disregarded.

Polyprotic bases are those bases that can neutralize more than one proton per molecule of base. This means they dissociate in or react with water to produce more than one OH^- ion per molecule. Polyprotic bases are much less common than polyprotic acids. They are treated in an analogous manner.

The Relationship between Structure and Acid-Base Strength

Study Section 15.9 in your textbook. You should have an overall idea of the relationship between structure and strength. In some cases, it is clear that bond strength governs this relationship. Hence HF is a weak acid, since it has the strongest bond of the hydrogen halides. In other cases, it is the electronegativity differences within the molecule that govern acid or base strength. Sometimes the acid or base strength depends on the structure of the corresponding conjugate base or acid. At this stage it is sufficient for you to have an understanding that more than one factor is often necessary to explain acid or base strength. You should also understand the trends in acid and base strength shown in the periodic table. Carefully consider the examples given in this section. In particular, work through Example 15.12 and its practice exercise.

# Acid-Base Properties of Salts

Study Section 15.10 in your textbook.

Salts That Produce Neutral Solutions

These are from strong acid and strong base neutralization.

Salts That Produce Basic Solutions

Acetic acid is a weak acid. The conjugate base of acetic acid is the acetate anion, CH_3COO^-. The conjugate base of a weak acid is strong enough to accept protons from water molecules, resulting in an excess of OH^- ions over H^+ ions.

If sodium acetate, a salt formed from the strong base NaOH and the weak acid CH_3COOH, is dissolved in water, it ionizes:

$$CH_3COONa + H_2O \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$$
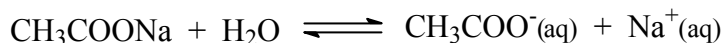
The Na^+ ion does not react further. It does not react with water to reform NaOH since NaOH is a strong base and remains totally dissociated. In other words, the following does not occur.

$$Na^+ + H_2O \overset{\times}{\rightleftharpoons} NaOH + H^+$$
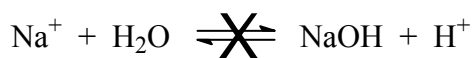
However, the acetate ion is the conjugate base of a weak acid and does react further with water.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$
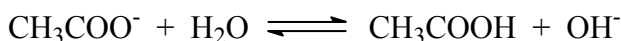
Here the acetate ion acts as a proton sink and accepts a proton from a water molecule to form acetic acid (see Figure 4.1 in this unit). This leaves an OH^- ion, and so the solution is basic. *Salts of weak acids / strong bases are basic.* (Or, in solution, conjugate bases of weak acids are basic.) The reaction of a conjugate base such as shown in this last equilibrium is sometimes called a **hydrolysis** reaction. This might imply that ionic acids and bases somehow react differently to non-ionic acids and bases. They do not; overall there is the same competition between two bases for the proton. For the reaction above of CH_3COO^- and water, the equilibrium expression is

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-][H_2O]}$$

The K_b is the equilibrium constant for the reaction of the conjugate base of the weak acid CH_3COOH. If you are not given equilibrium constants for conjugate bases of weak acids, you can work them out easily by using the relationship $K_w = K_aK_b$, developed in Section 15.7 of your textbook. Calculations on salts of weak acids / strong bases involve the same equilibrium principles as before, and once again it is usually possible to use the approximation method. Now work through Example 15.13 in your textbook and its practice exercise, and then try the following calculation.

Problem: Calculate the pH of a solution of 0.010 M sodium urate. The K_a for uric acid is 1.3×10^{-4}.

Solution: This calculation involves the salt of a weak acid, uric acid, and a strong base, NaOH. When sodium urate dissolves in water it dissociates into Na^+ ions and urate ions.

(For convenience, we designate the urate ion as Ur^-, since the actual formula for uric acid or the urate ion is irrelevant here.) Ur^- ions (the conjugate base of the weak acid) are stronger bases than water. Protons are pulled off water by Ur^-, leaving an excess of OH^- ions.

$$Ur^- + H_2O \rightleftharpoons HUr + OH^-$$
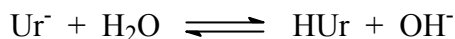
The solution will be basic, as you would expect for the salt of a strong base/weak acid. The equilibrium expression for this equilibrium is

$$K_b = \frac{[HUr][OH^-]}{[Ur^-]}$$

The tabulated concentrations are as follows.

	$[Ur^-]$	$[HUr]$	$[OH^-]$
Start	0.010	–	–
Equilibrium	$0.010 - x$	x	x

(Remember that the molarity of pure water is a constant and contained in the value for K_b. It does not need to appear in the equilibrium expression.) Substituting into the equilibrium expression gives

$$K_b = \frac{(x)(x)}{(0.010 - x)} = \frac{K_w}{K_a}$$

The equilibrium constant, K_b, for the conjugate base Ur^- is not given, but you can work it out using $K_b = K_w / K_a$. In this case,

$$K_b = 10^{-14} / 1.3 \times 10^{-4} = 7.7 \times 10^{-11}$$

K_b is very small, so the reaction lies very much to the left. This means that x is very small and $(0.010 - x)$ approximately equals 0.010. The calculation now becomes

$$\frac{x^2}{0.010} = 7.7 \times 10^{-11}$$

so

$$x = \sqrt{7.7 \times 10^{-13}} = 8.8 \times 10^{-7}$$

Check: 8.8×10^{-7} is much less than 5% of 0.010, and $x = [\text{OH}^-]$, so

$$\text{pOH} = -\log(8.8 \times 10^{-7}) = 6.06$$

$$\text{pH} = 14.00 - 6.06 = 7.94$$

The solution of 0.010 M sodium urate is basic, as expected.

Salts That Produce Acidic Solutions

In an analogous manner, it can be shown that the conjugate acid of a weak base undergoes hydrolysis with water, resulting in acidic solutions. Work through the following problem, where the conjugate acid of the weak base ammonia produces an acidic solution.

Problem: Calculate the pH of a solution of 0.050 ammonium chloride.

Solution: Ammonium chloride is the salt of the weak base ammonia, NH_3, and the strong acid HCl. In aqueous solution, chloride ions, Cl^-, do not react with water to reform HCl. (Chloride ions are weaker bases than water.) However, the conjugate acid of ammonia, NH_4^+, is a stronger acid than water. Thus, protons from NH_4^+ fall to the proton sink, H_2O (see Figure 4.1 in this unit).

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$
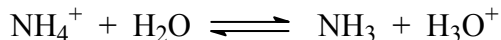
This gives an acidic solution. *Salts of weak bases / strong acids are acidic.* (Or, in solution, conjugate acids of weak bases are acidic.) The equilibrium expression is

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

The tabulated concentrations are

	$[NH_3]$	$[H_3O^+]$	$[NH_4^+]$
Start	–	–	0.050
Equilibrium	x	x	$0.050 - x$

Substituting into the equilibrium expression gives

$$K_a = \frac{(x)(x)}{(0.050 - x)} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Equilibrium constants for conjugate acids of weak bases are not given but can be calculated from $K_a = K_w / K_b$. The K_b value for ammonia, 1.8×10^{-5}, is given in Table 15.4 of your textbook.

Since the calculated K_a value for NH_4^+ is very small, the equilibrium lies very much to the left. Thus x, the concentration of H_3O^+ formed during hydrolysis, is very small, and $0.050 - x$ is approximately 0.050.

$$\frac{x^2}{0.050} = 5.6 \times 10^{-10}$$

$$x = \sqrt{5.6 \times 10^{-10} \times 0.050} = 5.3 \times 10^{-6}$$

Check: 5.3×10^{-6} is smaller than 5% of 0.050. Thus,

$$[H_3O^+] = 5.3 \times 10^{-6},$$

$$pH = -\log (5.3 \times 10^{-6}) = 5.28.$$

Example 15.14 in your textbook is very similar to this last problem. Follow through its solution and then try the practice exercise yourself.

As you followed through these problems you may have seen a similarity to the calculations for weak acids and weak bases. Again, it is possible to reduce the amount of time required for such a calculation by using a general formula. For the solution of a salt of a weak acid/strong base,

$$[OH^-] = \sqrt{\frac{K_w}{K_a} \times \text{salt conc.}} \quad \text{i.e., a basic solution}$$

For the solution of a salt of a weak base / strong acid,

$$[H_3O^+] = \sqrt{\frac{K_w}{K_b} \times \text{salt conc.}} \quad \text{i.e., an acidic solution}$$

If you choose to use these formulas (and they can save you a lot of time) you should make sure that you know *why* they work and *when* they are applicable.

The metal cations Al^{3+}, Cr^{3+}, Fe^{3+}, Bi^{3+}, and Be^{2+} also produce acidic solutions in water, as discussed in your textbook.

Salts in Which Both the Cation and the Anion Hydrolyze

These can give acidic, basic, or neutral solutions in water, depending on the K_a and K_b values for the conjugate acid and base involved. You are not required to do calculations on these amphoteric species, that is, substances that can act as both acid and base, but you must be able to predict if the solution is acidic, basic, or neutral.

Acid-Base Properties of Oxides and Hydroxides

Read Section 15.11 in your textbook.

You do not have to memorize the oxide formulas given in Figure 15.8 in your textbook, however, you should know that metallic oxides react with water to form basic hydroxides, that non-metallic oxides in water produce acids, and what is meant by an amphoteric species.

Lewis Acids and Bases

Study Section 15.12 of your textbook.

An extended category of acids and bases is **Lewis acids and bases**. You should know these definitions and understand that while all Lewis bases are also classified as Brønsted bases, not all Lewis acids are Brønsted acids. This difference comes out of the definitions. If a species can accept a proton (Brønsted base), it does so by donating an electron pair (Lewis base). But just because a species can accept an electron pair (Lewis acid), this does not necessarily mean it has a proton to donate (Brønsted acid). Make sure you understand this distinction. Your textbook gives a number of examples of how compounds act as Lewis acids and bases. You will have encountered the terms *Lewis acids and bases* and also the terms *electrophile* and *nucleophile* in CHEM 1503. If you continue your studies in chemistry, you will find that these terms are in common use.

Now work through Example 15.15 in the textbook and its practice exercise.

Use the summary at the end of Chapter 15 to review the important acid-base concepts discussed above.

The Common Ion Effect

Study Sections 16.1 and 16.2 of your textbook. The **common ion effect** is a specific application of Le Chatelier's principle. Make sure you can derive the **Henderson-Hasselbalch equation**. This equation is sometimes written as

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

since the conjugate base (of the weak acid involved) is obtained from the salt of that weak acid. Work through Example 16.1 in your textbook and its practice exercise. For the common ion effect with a weak base and the salt of that weak base, this unit takes a slightly different approach to the one described in your textbook. The following derivation parallels the weak acid / salt of weak acid method explained in Section 16.2.

Consider a weak base, B.

$$\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^-$$
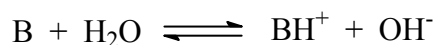
The ionization constant for this equilibrium is

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

On rearrangement this becomes

$$[OH^-] = K_b \times \frac{[B]}{[BH^+]}$$

In the presence of added BH^+ (from the salt of the weak base / strong acid, BHCl), the weak base equilibrium is shifted to the left. The equilibrium concentration of the weak base, B, can be approximated by the original base concentration. The equilibrium concentration of the conjugate acid, BH^+, can be approximated by the concentration of the salt. Thus

$$[OH^-] = K_b \times \frac{[B]}{[BH^+]}$$

becomes

$$[OH^-] = K_b \times \frac{[base]}{[conjugate\ acid]}$$

Taking the negative logarithm of both sides results in

$$pOH = pK_b + \log \frac{[conj.\ acid]}{[base]} \quad or \quad pOH = pK_b + \log \frac{[salt]}{[base]}$$

Of course, to find the pH of this solution you would use $pH = 14 - pOH$. This version of the Henderson-Hasselbalch equation is essentially the same as the equation

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$

derived at the end of Section 16.2. In this unit, we use

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

in doing calculations of solutions containing weak bases and their conjugate acids.

Buffers

Study Section 16.3 in your textbook. This is an important topic, so take the time to really understand the chemistry and arithmetic in this section. An **acid buffer** usually consists of a solution of a weak acid and the salt of that weak acid. Some examples are:

- acetic acid and sodium acetate
- formic acid and sodium formate
- nitrous acid and potassium nitrite

Note that the salt is that of the weak acid and a strong base. A **basic buffer** usually consists of a solution of a weak base and the salt formed from that weak base. Some examples are:

- ammonia and ammonium chloride
- nicotine and nicotine hydrochloride
- hydrazine and hydrazine nitrate

Work through Examples 16.2 and 16.3 from your textbook, and their practice exercises. The following problem involves a basic buffer.

Problem: Calculate the pH of a buffer solution prepared by dissolving 40.2 g of NH_4Cl and 20.3 g of NH_3 in enough water to form 1.0 L of solution.

Solution: This solution contains a weak base (NH_3) and the salt of a weak base–strong acid (NH_4Cl). This is a basic buffer so

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$= pK_b + \log \frac{[NH_4^+]}{[NH_3]}$$

K_b of NH_3 is 1.8×10^{-5}, so

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

But $\qquad\qquad\qquad [NH_4^+] = 40.2 \text{ g} / 53.5 \text{ g mol}^{-1} = 0.751 \text{ M}$

and $\qquad\qquad\qquad [NH_3] = 20.3 \text{ g} / 17.0 \text{ g mol}^{-1} = 1.19 \text{ M}$

so $\qquad\qquad\qquad pOH = 4.74 + \log(0.751/1.19)$

$$= 4.74 - 0.200$$

$$= 4.54$$

and $\qquad\qquad\qquad pH = 14 - 4.54 = 9.46$

If you had used the formula for a basic buffer given at the end of Section 16.2, the solution would be

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{conjugate acid}]}$$

As K_b for the weak base, NH_3, is 1.8×10^{-5}. K_a for its conjugate acid is

$$\frac{(1.0 \times 10^{-14})}{(1.8 \times 10^{-5})} = 5.6 \times 10^{-10}$$

$\text{p}K_b$ for NH_3 is 4.74, so $\text{p}K_a$ for its conjugate acid, NH_4^+, is

$$14.00 - 4.74 = 9.26$$

then using $\text{pH} = \text{p}K_a + \log \dfrac{[\text{base}]}{[\text{conjugate acid}]}$

$$= 9.26 + \log\left(\frac{1.19}{0.751}\right)$$

$$= 9.26 + 0.200$$

$$= 9.46$$

Example 16.3 shows how a buffer resists ("buffers" against) large changes in pH when hydrogen ions are added to the solution. If hydroxide ions had been added to the buffer solution in 16.3, the pH would have increased only slightly, as shown in the following.

Problem: A buffer system consisting of 1.00 M CH_3COOH and 1.00 M CH_3COONa has a pH of 4.74. Determine the pH after 0.10 moles of solid NaOH is added to 1.00 L of the buffer solution.

Solution:

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$
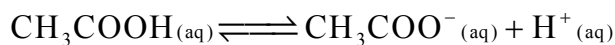
The addition of NaOH provides OH^- ions, which are then used up by the reaction

$$H^+ + OH^- \longrightarrow H_2O$$
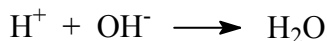
Thus, the acetic acid ionization equilibrium moves to the right. So

$$[CH_3COOH] = 1.00 - 0.10 = 0.90$$

$$[CH_3COO^-] = 1.00 + 0.10 = 1.10$$

Using the Henderson-Hasselbalch equation, the pH for the solution is

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} = 4.74 + \log \frac{1.10}{0.90} = 4.83$$

A buffer solution has the best buffering capacity when the ratio of acid to salt (or base to salt) is 1:1. However, as long as this ratio is in the range of 1:10 to 10:1, the solution is still practical for most purposes. Outside of this range, additions of small amounts of acid or base can quickly use up all the salt (that is, all the conjugate base or conjugate acid).

The pH will then change significantly. In such a case, you would have *exceeded the buffer capacity*. This buffer range is illustrated for an acetate buffer in Figure 4.2 below.
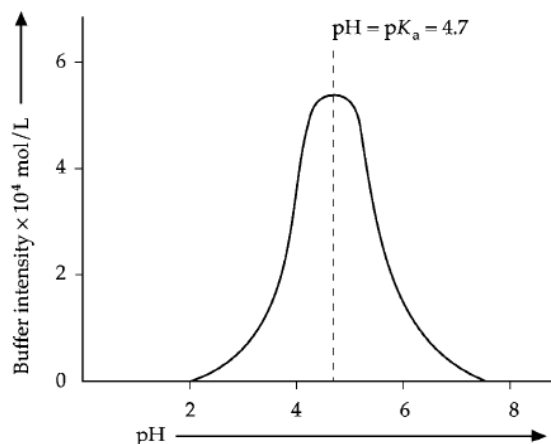

Figure 4.2: Relative buffer capacity of 10^{-3} M acetate buffer solution as a function of pH.

The following problem demonstrates a case where buffer capacity is exceeded.

Problem: Calculate the pH when 1.00 g of solid NaOH is added to one litre of a buffer solution containing 0.0380 moles of CH_3COONa and 0.0210 moles of CH_3COOH.

Solution: The pH of the buffer solution is

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} = 4.74 + \log \frac{0.0380}{0.0210} = 5.00.$$

The addition of 1.00 g / 40.0 g mol^{-1} = 0.0250 moles of OH$^-$ from NaOH forces the equilibrium

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$
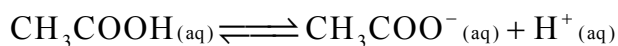
to the right. OH$^-$ ions combine with the H$^+$ ions as

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

In effect, this removes H^+ ions from solution. Thus, more CH_3COOH dissociates (Le Chatelier's principle). The new number of moles of salt and acid are now
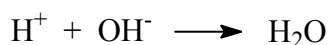
$$salt = 0.0380 + 0.0250 = 0.0630 \text{ moles}$$

$$acid = 0.0210 - 0.0250 = \text{a negative value!}$$

This means all the weak acid is neutralized—a buffer no longer exists (the buffer capacity has now been exceeded). The pH of the solution is now estimated from the added strong base remaining:

$$0.0250 \text{ moles base initially} - 0.0210 \text{ moles neutralized}$$

$$= 0.0040 \text{ moles of NaOH in 1 L of solution}$$

$$[OH^-] = 0.0040 M$$

$$pOH = 2.40 \text{ and } pH = 11.60$$

Buffer action is not only associated with weak acids and bases. As shown in Figure 4.3 below, strong acid–strong base systems are slightly better buffers than weak acid–strong base systems. However, the pH range of the buffering action is either very high or very low with strong acid–strong base systems. Thus, these are not generally used or considered as buffer systems.
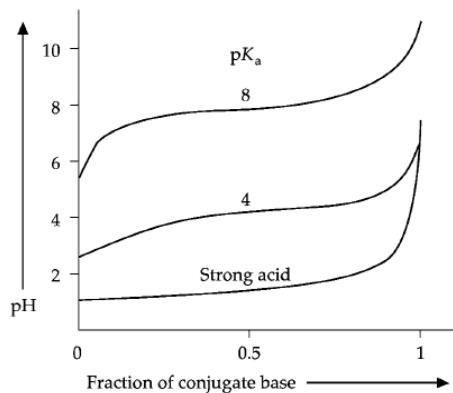
Figure 4.3: Variation in pH with change in the fraction of conjugate base.

Preparing Buffer Solutions

In addition to being able to calculate the pH of a given buffer solution, you must be able to work out the amount of weak acid and its conjugate base (or weak base and its conjugate acid) that will produce a solution of the required pH. Since the pK_a (or pK_b) value of the particular weak acid (or base) is fixed, the final pH of the buffer depends on the ratio

$$\frac{[salt]}{[acid]} \quad \text{or} \quad \frac{[salt]}{[base]}$$

Note that the addition of water does not change the pH of the buffer solution. A change in volume affects the concentration of the acid in the same way as the concentration of the salt. The pH depends on the *ratio* of these concentrations. The following problem demonstrates one way to prepare a buffer solution.

Problem: How would you prepare one litre of a buffer solution of pH 5.00 using 0.100 M acetic acid and solid sodium acetate?

Solution: This is an acidic buffer, so use the formula

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

For acetic acid, $K_a = 1.8 \times 10^{-5}$ and $pK_a = 4.74$. Substituting into the Henderson-Hasselbalch equation gives

$$\log \frac{[salt]}{[acid]} = 5.00 - 4.74 = 0.26$$

so

$$\frac{[salt]}{[acid]} = 1.82.$$

This means that you must have 1.82 times as much salt as acid. One litre of 0.100 M acetic acid contains 0.100 moles of acid. Thus,

$$\text{Moles of salt required} = 0.100 \times 1.82 = 0.182$$

$$\text{and mass of salt required} = 0.182 \text{ mol} \times 82.0 \text{ g mol}^{-1}$$

$$= 14.9 \text{ g } CH_3COONa$$

To make a litre of buffer solution of pH 5.00, add 14.9 g of sodium acetate to one litre of 0.100 M acetic acid.

You can also prepare a buffer solution from the partial neutralization of a weak acid by a strong base. Such calculations involve a bit more chemistry and some further stoichiometry, but the actual pH calculation is unchanged.

Problem: How would you prepare one liter of a buffer solution of pH 5.00 using 0.100 M acetic acid and 0.100 M sodium hydroxide?

Solution: In this calculation you prepare the salt of the weak acid from partial neutralization of the weak acid. As above, the pK_a of acetic acid is 4.74 and, from the Henderson-Hasselbalch equation, the ratio of salt to acid is 1.82 to 1. (Or the [acid]:[salt] ratio is 0.549:1.)

Let the volume of sodium hydroxide added to make the buffer solution be x mL. Then the volume of sodium acetate formed is x and the volume of acetic acid neutralized is x. Thus, the volume of acetic acid remaining unneutralized is $0.549x$. The total volume of acetic acid used is

$$x \text{ (neutralized)} + 0.549x \text{ (left unneutralized)},$$

the volume of base used is x, so the total volume of the solution is

$$x + 0.549x = x = 1.00 \text{ L}$$

and $$x = 1.00 / 2.549 = 392 \text{ mL}$$

Use 392 mL of 0.100 M NaOH and 1.00 L – 392 mL = 608 mL of 0.100 M acid.

Check: 392 mL of sodium acetate and 608 – 392 = 216 mL (or 0.549 × 392 mL) acid implies

$$pH = 4.74 + \log(392/216)$$

$$= 4.74 + \log 1.81$$

$$= 4.74 + 0.26 = 5.00$$

Now work through Example 16.4 in your textbook and its practice exercise.

A General Approach to Acid-Base Calculations

Table 4.1 in this unit summarizes the different types of acid-base calculations you are likely to encounter. The table lists the acid category first, with the analogous base in brackets in the same category. While not absolutely all calculations can be classified into one of the six categories given here, nevertheless, you will find this table very helpful. Most students tend to feel a little overwhelmed at this stage of acid-base calculations. "If I just knew how to start, I'd be okay," is a typical comment from many students. So this table attempts to get you over the *Where do I start?* syndrome. You have to start by determining what you have in the solution. If the solution is a weak acid, you are considering a type 2 (on Table 4.1) calculation. If you have a mixture of hypochlorous acid and potassium hypochlorite, for instance, first consult Table 4.2 in this unit, which tells you that hypochlorous acid is a weak acid. Since potassium hypochlorite is the salt formed from the neutralization of a weak acid (hypochlorous) and a strong base (KOH), this solution contains a weak acid and the salt of that weak acid. The solution is a type 5: an acidic buffer.

There are a couple of things to remember if you are using Table 4.1 from this unit to help you decide on an approach to a problem. First, you cannot determine a calculation type until you have neutralized all possible acid with available base. This means that a solution of 25 mL of 0.1 M HCl with 25 mL of 0.1 M NaOH is not a type 1 calculation.

Complete neutralization occurs to form the salt of a strong acid–strong base. This is a type 3 calculation (hardly a calculation—at 25ºC all such solutions have pH 7 regardless of their concentration). The second thing to remember is that you cannot use this table unless you determine that the solution is *one and only one* type. For example, a solution that is 0.1 M in HCl and 0.5 M in acetic acid looks as if you have a mixture of types 1 and 2. This is not possible using this table.

You have to decide which type the solution can be categorized as. HCl is a strong acid and totally dissociated. The H^+s from HCl will suppress the dissociation of the weak acid CH_3COOH. Thus, the H^+ can be considered to be due solely to HCl. The solution is categorized as a type 1.

You will not find this method in a textbook. When this unit refers to type 4 or type 6, it is referring only to the summary in Table 4.1 *in this unit*. This is one way of helping students get started on pH calculations. It is not a universal system, nor is it supposed to replace an understanding of the equilibrium principles involved in acid-base chemistry. If you find another person who understands that type 5 refers to buffers, you are no doubt talking to one of this course writer's former students! Use Table 4.1 as an aid in acid-base calculations, but do not assume that it will do everything for you.

Table 4.1: Types of acid-base calculations.

Type	Generalized Formula	Examples	Comments
1. Strong acid (strong base)	$[H^+] =$ molarity ($[OH^-] =$ molarity)	HCl, HNO_3 (NaOH, KOH)	pH dependent on concentration
2. Weak acid (weak base)	$[H^+] = \sqrt{K_a[\text{acid}]}$ ($[OH^-] = \sqrt{K_b[\text{base}]}$)	acetic acid, HF (NH_3, morphine)	pH dependent on concentration
3. Salt of strong acid–strong base	$[H^+] = 10^{-7}$	NaCl	pH independent of concentration
4. Salt of weak acid–strong base (Salt of strong acid–weak base)	$[OH^-] = \sqrt{K_w/K_a[\text{salt}]}$ ($[H^+] = \sqrt{K_w/K_b[\text{salt}]}$)	sodium acetate (ammonium chloride)	pH dependent on concentration. Ionic weak bases and acids; conjugate species
5. Weak acid + salt of weak acid–strong base (Weak base + salt of weak base–strong acid)	$pH = pK_a + \log[\text{salt}]/[\text{acid}]$ ($pOH = pK_b + \log[\text{salt}]/[\text{base}]$)	acetic acid + sodium acetate (ammonia + ammonium chloride)	Buffers! pH independent of concentration
6. Salt of weak acid–weak base	not required	ammonium acetate	amphoteric species

The following problem shows how you can use Table 4.1 in this unit.

Problem: For each of the following mixtures, determine the appropriate Table 4.1 category (type).

a.   25 mL of 0.1 M HCl and 50 mL of 0.05 M NH_3

b.   100 mL of 0.087 M KNO_3 and 22 mL of water

c.   20 mL of 0.1 M HF and 15 mL of 0.1 M NaOH

d.   30 mL each of 0.5 M HCl and 0.5 M NaCl

e.   30 mL of 0.05 M HCl and 30 mL of 0.05 M KOH

f.   45 mL of 0.07 M NH_3 and 12 mL of 0.5 M NaCl

Solution: First determine if and how much neutralization is possible in each mixture.

a.   This is a mixture of a strong acid and a weak base so neutralization will occur. There is twice the volume of weak base (NH_3) at double the concentration, so total neutralization occurs. You can also work this out mathematically using

$$(M_{acid})(V_{acid}) = (M_{base})(V_{base})$$
$$0.1 \times 25 = 0.05 \times 50$$

The result is a solution of the salt of a strong acid–weak base. This is a type 4 calculation.

b.   This is the salt of a strong acid (HNO_3) and a strong base (KOH). The addition of water does not change the pH of 7 in this type 3 calculation.

c.   This is a solution of a weak acid and a strong base. Incomplete neutralization occurs as follows:

20 mL of 0.1 M HF plus 15 mL of 0.1 M NaOH is equivalent to 15 mL of 0.1 M NaF plus 5 mL of 0.1 M HF all diluted to 35 mL (only 15 of the 20 mL of HF is neutralized).

This solution now contains a weak acid (HF) and the salt of that weak acid (NaF).

Therefore, it is an acidic buffer; type 5 calculation.

d.   This solution contains a strong acid (HCl) and the salt of a strong acid–strong base (NaCl). The salt of the strong acid–strong base makes no contribution to solution pH. Thus, this is a strong acid calculation; type 1.

e.   30 mL of 0.05 M HCl plus 30 mL of 0.05 M KOH is equivalent to 30 mL of 0.05 M KCl diluted to a total volume of 60 mL. KCl is the salt of a strong acid–strong base. This is a type 3 calculation (pH = 7).

f.   This mixture contains a weak base (NH_3) and the salt of a strong acid–strong base (NaCl). The salt makes no contribution to the solution pH. Thus, solution pH depends only on the diluted weak base; a type 2 calculation.

Table 4.2 in this unit is a summary of K values for weak acids and weak bases. Note that this table gives the K_a value for the weak acid and the K_b value for the conjugate base of that weak acid. As you can see from these values, $K_a \times K_b = K_w$. For example, use the K_a value for acetic acid and the K_b value for its conjugate base acetate, $C_2H_3O_2^-$. Then $(1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 10^{-14}$. If you look closely at Table 4.2, it should help you to realize that acids and bases, whether strong or weak, neutral, ionic, organic, or inorganic, are not different entities in terms of acid-base chemistry. They are related species.

Neutralization and pH Titration Calculations

Study Section 16.4 in your textbook. Follow through the explanations in this section and work through Examples 16.5 and 16.6 and their practice exercises. You should recognize that these are not new concepts, but applications of the theory that you have already learned.

There are two things to remember when dealing with equivalence points. The first is that an equivalence point of a titration is not necessarily at pH 7. For this reason it may be better to refer to **equivalence point** rather than to **neutralization point**. (The term *neutral* may lead you to expect pH 7.) The equivalence point occurs at that point of a titration where the exact number of moles of OH^- ions have been added as H^+ ions were available (or vice versa). This will only be at pH 7 for reactions involving strong acids and strong bases at 25ºC. For weak acid–strong base titrations, the equivalence point is basic. For strong acid–weak base titrations, the equivalence point is acidic. The second thing to remember is that in neutralization problems you have to account for the concentration of the salt. A salt formed from the neutralization of 100 mL of 0.1 M of weak acid and 100 mL of 0.1 M strong base will have a concentration of 0.05 M in 200 mL volume.

Table 4.2: Dissociation constants of weak acids and weak bases.

	Acid	K_a	Base	K_b
Acetic acid	$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^-$	5.6×10^{-10}
Ammonium ion	NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
Anilinium ion	$C_6H_5NH_3^+$	2.6×10^{-5}	$C_6H_5NH_2$	3.8×10^{-10}
Benzoic acid	$HC_7H_5O_2$	6.5×10^{-5}	$C_7H_5O_2^-$	1.5×10^{-10}
Boric acid	H_3BO_3	5.8×10^{-10}	$H_2BO_3^-$	1.7×10^{-5}
Carbonic acid	H_2CO_3	4.2×10^{-7}	HCO_3	2.4×10^{-8}
	HCO_3^-	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}
Cyanic acid	HCNO	3.5×10^{-4}	CNO^-	2.9×10^{-11}
Ethylammonium ion	$C_2H_5NH_3^+$	1.8×10^{-11}	$C_2H_5NH_2$	5.6×10^{-4}
Formic acid	$HCHO_2$	1.7×10^{-4}	CHO_2^-	5.9×10^{-11}
Hydrazinium ion	$N_2H_5^+$	5.9×10^{-9}	N_2H_4	1.7×10^{-6}
Hydrocyanic acid	HCN	4.9×10^{-10}	CN	2.0×10^{-5}
Hydrofluoric acid	HF	7.1×10^{-4}	F^-	1.4×10^{-11}
Hydrogen sulfide	H_2S	9.5×10^{-8}	HS^-	1.1×10^{-7}
	HS^-	1.0×10^{-19}	S^{2-}	1.0×10^{5}
Hypochlorous acid	HClO	3.2×10^{-8}	ClO^-	3.1×10^{-7}
Hydroxylammonium ion	NH_3OH^+	9.1×10^{-7}	NH_2OH	1.1×10^{-8}
Methylammonium ion	$CH_3NH_3^+$	2.3×10^{-11}	CH_3NH_2	4.4×10^{-4}
Nitrous acid	HNO_2	4.5×10^{-4}	NO_2^-	2.2×10^{-11}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}
	$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}
	HPO_4^{2-}	4.8×10^{-13}	PO_4^{3-}	2.1×10^{-2}
Propionic acid	$HC_3H_5O_2$	1.4×10^{-5}	$C_3H_5O_2^-$	7.1×10^{-10}
Pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	C_5H_5N	1.7×10^{-9}
Pyruvic acid	$HC_3H_3O_3$	1.4×10^{-4}	$C_3H_3O_3^-$	7.1×10^{-11}
Oxalic acid	$H_2C_2O_4$	6.5×10^{-2}	$HC_2O_4^-$	1.5×10^{-13}
	$HC_2O_4^-$	6.1×10^{-5}	$C_2O_4^{2-}$	1.6×10^{-10}
Hydrogen sulfate	HSO_4^-	1.3×10^{-2}	SO_4^{2-}	7.7×10^{-13}
Sulfurous acid	H_2SO_3	1.3×10^{-2}	HSO_3^-	7.7×10^{-13}
	HSO_3^-	6.3×10^{-8}	SO_3^{2-}	1.6×10^{-7}
Aquo ferric ion	$[Fe(H_2O)_6]^{3+}$	6.3×10^{-3}	$[Fe(H_2O)_5(OH)]^{2+}$	1.58×10^{-12}
Aquo aluminum ion	$[Al(H_2O)_6]^{3+}$	1.3×10^{-5}	$[Al(H_2O)_5(OH)]^{2+}$	7.7×10^{-10}

You will be able to practise the technique of titration during your laboratory experiments. In fact, you will do a number of titrations in your experiments. In Unit 6 of this course, you will encounter oxidation-reduction titrations.

The technique is similar for both types and you should understand the stoichiometry involved. For acid-base neutralizations the reaction is

$$H^+ + OH^- \longrightarrow H_2O$$
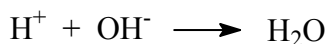
and all acid-base neutralizations are based on this equation, regardless of whether the acids and bases are strong or weak.

Note that although a 0.1 M solution of a strong acid has a higher concentration of hydrogen ions (lower pH) than a 0.1 M solution of a weak acid, equal volumes of these solutions require the same amount of base for neutralization. This is because a 0.1 M solution has potentially the same number of H^+ ions. As base is added to a weak acid solution, the H^+ ions react with OH^- ions to form water. In effect, this removes H^+ from the solution and more of the weak acid is dissociated. Eventually, at the equivalence point, all the weak acid is "consumed," or converted to its conjugate base.

A **titration** is the process of converting an acid into its conjugate base. This requires adding an amount of a proton acceptor (OH^-) that depends on the quantity of the acid present, not on its strength. As noted earlier, a titration does not necessarily result in a neutral solution. In this respect, the term *neutralization* is misleading. A weak acid is said to be "neutralized" when enough base is added to totally convert the acid to its conjugate base. This conjugate base will accept some protons from water, leaving some OH^- ions. The extent of this hydrolysis is small but the equivalence point is no longer neutral.

For acids with more than one proton per molecule to donate (polyprotic acids), the stoichiometry of neutralization still depends on the $H^+ + OH^- \rightarrow H_2O$ reaction. A 0.1 M solution of H_2SO_4 requires twice the volume of base for neutralization compared to a 0.1 M HCl solution, since H_2SO_4 has twice as many protons as HCl. Similarly, H_3PO_4 has three times the number of protons to donate as HCl.

In the laboratory you can also follow the course of an acid-base titration using a pH meter. A graph of solution pH versus mL of added base (or acid) is known as a pH titration curve. It is possible to calculate the points on such a curve and produce theoretical pH titration curves. Such an exercise shows you how individual pH calculations can be used.

Problem: Construct a titration curve for the neutralization of 100 mL of 0.10 M acetic acid (CH_3COOH) against added 0.10 M NaOH. Indicate on the completed graph, the equivalence point and the half-equivalence point, and circle the buffer region.

Solution: The points calculated are shown on the graph in Figure 4.4 in this unit. When constructing such titration curves, you should always graph the results on proper graph paper.

Although you can choose any number of points to calculate, the very minimum number is five. The first five points, calculated below, are essential. K_a for acetic acid is 1.8×10^{-5} (from Table 15.3 in your textbook).

1. 0 mL of 0.10 M NaOH added to the 100 mL of 0.10 M acetic acid. This is the initial point on the graph, before any neutralization by base. This is just a weak acid calculation (type 2). We find

$$[H^+] = \sqrt{K_a \times [\text{acid}]}$$

$$= \sqrt{1.8 \times 10^{-5} \times 0.10}$$

$$= 1.3 \times 10^{-3}$$

Check: 5% of 0.1 is 5×10^{-3}, so the assumption is valid

$$pH = 3 - \log 1.3 = 2.89$$

2. 10 mL of 0.10 M NaOH added to the 100 mL of 0.10 M acetic acid. This amount of base will neutralize 10 mL of the weak acid. The result will be a solution of

    10 mL of Na acetate + 90 mL of unreacted acetic acid + 10 mL of H_2O

    This is a solution of weak acid and a salt of that weak acid, that is, an acid buffer (type 5 calculation). We find

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

$$= 4.74 + \log \left(\frac{10 \text{ mL}}{90 \text{ mL}} \right)$$

$$= 4.74 - 0.95 = 3.79$$

Note that in a buffer calculation the volume ratio for [salt]/[acid] can be used if both have the same molarity (0.10 in this case). Nor do you have to account for the total volume of solution of 110 mL, since in a buffer added water dilutes the salt term as much as the acid term. This can be shown mathematically as

$$[salt] = \frac{0.10\,M \times 10\,mL}{110\,mL} \quad and \quad [acid] = \frac{0.10\,M \times 90\,mL}{110\,mL}$$

so the ratio of [salt]/[acid] is

$$\frac{0.10\,M \times 10\,mL}{110\,mL} \quad x \quad \frac{110\,mL}{0.10\,M \times 90\,mL}$$

This, of course, is the direct volume ratio. In remaining problems, we will use this direct volume ratio where appropriate.

3. 50 mL of 0.10 M NaOH added to the 100 mL of 0.10 M acetic acid. This amount of base will neutralize half of the weak acid. The solution can now be considered to be

    50 mL of 0.10 M Na acetate + 50 mL of acetic acid + 50 mL of H_2O

    This is a mixture of a weak acid and the salt of that weak acid, again an acid buffer.

    We find

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

    $$= 4.74 + \log \frac{50 \text{ mL}}{50 \text{ mL}} = 4.74$$

    This is the mid-equivalence (or mid-neutralization) point. Note that in a weak acid–strong base titration, *the* pH *at mid-equivalence* p*oint equals* pK_a. For a strong acid–weak base titration, *the* pOH *at mid-equivalence point equals* K_b. This is one experimental method of determining K_a and K_b values.

4. 90 mL of 0.10 M NaOH added to the 100 mL of 0.10 M acetic acid. Now 90 mL of the weak acid is neutralized, giving

    90 mL of 0.10 M Na acetate + 10 mL of 0.10 M acetic acid + 90 mL of H_2O

    This is an acidic buffer mixture. We find

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

    $$= 4.74 + \log \frac{90 \text{ ml}}{10 \text{ mL}}$$
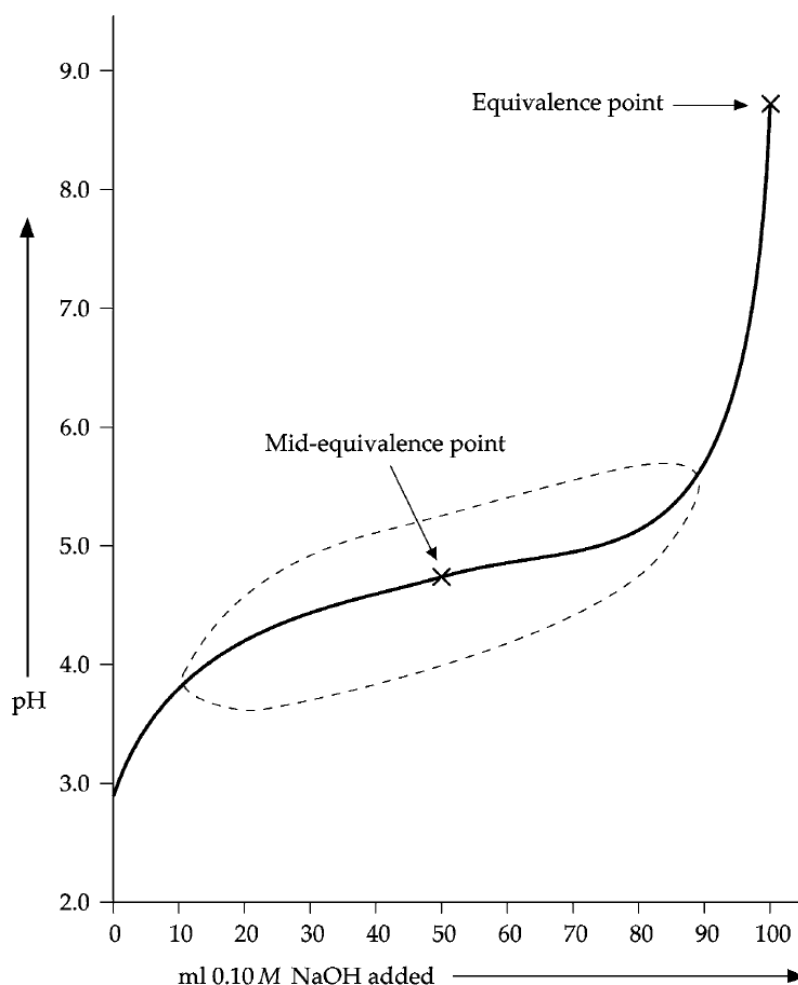
    $$= 5.69$$

Figure 4.4: Titration curve for 100 mL 0.10 M acetic acid against added 0.10 M NaOH solution. The dashed line (-----) circles the approximate buffer region.

5.   100 mL of 0.10 M NaOH added to the 100 mL of 0.10 M acetic acid. This amount of bases fully neutralizes all the acetic acid. This is the equivalence point. The solution now consists of 100 mL of 0.10 M Na acetate diluted to 200 mL (total volume). Na acetate is the salt of a weak acid–strong base; a type 4 (hydrolysis) calculation. Such a solution is basic. Using

$$[\text{OH}^-] = \sqrt{K_w / K_a \times [\text{salt}]}$$

$$= \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5}} \ x \ \frac{0.10\,M \times 100\,mL}{200\,mL}}$$

$$= 5.3 \times 10^{-6},$$

we find   pOH = 6 − log 5.3 = 5.28

and   pH = 8.72

These five points are the bare minimum necessary to outline the pH titration curve. You should always calculate:

- An initial point
- A mid-equivalence point
- An equivalence point
- A point at approximately 10% neutralization
- A point at approximately 90% neutralization

You can calculate further points if you desire, but these five will give you a reasonably accurate pH titration curve. The buffer region (circled in Figure 4.4) shows as fairly flat on the graph. This is where addition of base makes very little change to the pH. This is what you would expect of a buffer.

This has been quite a long explanation of these calculations and the graph, however, when you have had some practice at pH calculations, a similar exercise will not be as lengthy. Make sure you choose the buffer points carefully. At 25% and 75% neutralization, you would not be outlining the buffer region accurately. At 5% and 95%, you are outside the main buffer region. Further additions of 0.10 M NaOH to this 100 mL of 0.10 M acetic acid would be treated as a strong base (diluted) calculation.

Acid-Base Indicators

Study Section 16.5 in your textbook.

Experimentally, you determine an end-point of a titration. The end-point is approximately the same as the equivalence point, depending on the accuracy of the method of measurement. One common method of measuring an end-point is with a pH meter, an instrument which measures the electrical potential of a special electrode that is sensitive to the hydrogen ion concentration. It then converts it to a pH measurement as output. You may use such an instrument in the laboratory. A simpler, chemical method makes use of the fact that some complex organic acids have a different colour than that of their conjugate bases. These compounds are known as **indicators**. A list of common indicators is given in Table 16.1 of your textbook. The relative concentration of the indicator is always low since only one or two drops of the indicator solution are used. So the position of the equilibrium shown in the equation

$$HIn_{(aq)} \rightleftharpoons H^+_{(aq)} + In^-_{(aq)}$$
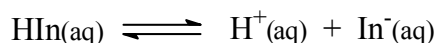
depends on the $[H^+]$ of the solution being determined. Work through Example 16.7 in the textbook and its practice exercise. You will have an opportunity in the laboratory course to use indicators.

pH and Slightly Soluble Ionic Compounds

Study Section 16.9 in your textbook.

The effect of pH on the solubility of a salt is another application of the common ion effect. Both slightly soluble metal hydroxides and salts that have a basic anion are more soluble at lower pH (greater H^+ concentration) and less soluble at higher pH (lesser H^+ concentration). Work through Examples 16.13 and 16.14 and their practice exercises.

Now read Section 16.11 in the textbook, which is especially important if you are also taking CHEM 1525, the associated laboratory course.

Use the summary at the end of Chapter 16 to review the important buffer and K_{sp} concepts discussed here.

Self-Assessment

Having reached the end of Unit 4, you should be able to:

- Define acids and bases using the Arrhenius, Brønsted, and Lewis theories.

- Write acid-base conjugate pairs for given compounds.

- Explain the relationship between structure and acid-base strength.

- Write equations and equilibrium expressions for aqueous solutions of acids and bases.

- Express $[H^+]$ as pH, pOH, or $[OH^-]$, and vice versa.

- Distinguish between weak and strong for acids and bases.

- Calculate the pH of solutions of weak acids or bases, or strong acids or bases, including polyprotic acids and bases.

- Explain why solutions of certain salts are acidic or basic and calculate the pH of solutions of such salts.

- Calculate the pH of buffer solutions, pH changes in buffer solutions, and methods of preparing buffers.

- Perform calculations relating solubility and pH.

- Construct pH titration curves.

- Explain the theory of acid-base indicators and their use.

Practice Exercise 4

Finish working through Unit 4 before you start this practice exercise which is found listed under the Practice Exercises section of course. The material in this unit is integrated throughout the practice exercises. The solutions to these problems will be provided once you have completed this practice exercise.

You may first want to try some of the supplementary exercises suggested under the next heading. However, if you feel that you have a reasonable understanding of the material, you can begin the practice exercise immediately. If you have no difficulties with this practice exercise, begin Assignment 4. If you feel that you need more practice, go to the Suggested Supplementary Exercises.

You should make a serious attempt to solve the practice exercise problems by yourself, using as a guide similar exercises from the textbook and from this unit. If your attempt is serious, you will learn a lot from the worked solutions in the Solutions to Practice Exercise 4 section of the Course Units.

Suggested Supplementary Exercises

At the end of each chapter in your textbook are further exercises on the material covered. We suggest that you do as many of these exercises as necessary. Doing such problems helps you understand and apply the principles involved in the concepts discussed. Fully worked solutions for most of the following exercises are given in the *Student Solutions Manual*. Most selected exercises at the ends of the chapters have their answers in the back of the textbook, or a solution method is described in the *Student Solutions Manual*.

You should make a serious attempt to solve a problem by yourself before looking at a worked solution.

From Chapter 15:

15.4, 15.5, 15.6, 15.16, 15.20, 15.24, 15.26, 15.33, 15.34, 15.35, 15.41, 15.44, 15.48, 15.52, 15.60, 15.62, 15.64, 15.68, 15.79, 15.80, 15.82, 15.88, 15.92, 15.102, 15.108, 15.137

From Chapter 16:

16.4, 16.7, 16.10, 16.13, 16.16, 16.18, 16.25, 16.28, 16.41, 16.67, 16.68, 16.70, 16.72, 16.87, 16.88, 16.89, 16.90, 16.91, 16.92, 16.113

Assignment 4

Now refer to your *Assignments* and complete Assignment 4. Consult your Course Guide for the week this assignment is due. Send the assignment to your Open Learning Faculty Member. You may send the assignment to your Open Learning Faculty Member using the assignment tool in Blackboard or by mail with a Marked Assignment Form. Be sure to keep a copy of the assignment—it will be useful if you wish to discuss your work with your Open Learning Faculty Member.