Lab #9
Studying the pH of Acid, Base, and Salt Solutions

Goals

Part A: **Acids and Bases**
- To understand the basic concepts underlying acid/base chemistry.
- To understand the differences between a strong acid and a weak acid.

Part B. **Water and the pH and pOH scales**
- To learn about water's acid/base nature
- To become familiar with the pH and pOH scales.

Part C. **Example Calculations –** To learn how to calculate theoretical pH and K_a

Part D: **In-Lab Portion –** To calculate the theoretical pH of strong and weak acid solutions; to calculate the K_a of a weak acid and to measure the pH of acid and salt solutions.

Part A: Acids and Bases

Acid-base reactions are among the most common in chemistry. These reactions are important in environmental chemistry (e.g. the formation of acid rain), organic chemistry (e.g. the synthesis of many chemicals), inorganic chemistry (e.g. the interaction of metal cations with water), and biochemistry (e.g. thousands of reactions in biological organisms). It is important to have a thorough understanding of the underlying concepts of acid-base chemistry.

There are several definitions for acids and bases. Our lab is focused on aqueous chemistry, so two definitions are particularly useful. Each definition is named after the scientists who first determined the theoretical basis of that acid/base chemical system.

Arrhenius Acids and Bases

The classical **Arrhenius**[1] (pronounced "are-ray-nee-us") definition is limited to aqueous solutions. An Arrhenius acid is a substance that produces hydronium ions (H_3O^+) in an aqueous solution. An Arrhenius base is a substance that produces hydroxide ions (OH^-) in an aqueous solution.

Brønsted-Lowry Acids and Bases

The broader **Brønsted-Lowry** definition is not limited to aqueous solutions. A Brønsted-Lowry acid is a proton (H^+) donor, and Brønsted-Lowry base is a proton acceptor. However, in an aqueous environment, the H^+ donated by a Brønsted-Lowry acid will covalently bond to a water molecule, forming a hydronium ion. This means that essentially any Arrhenius acid is also a Brønsted-Lowry acid. In contrast, Brønsted-Lowry bases are not necessarily bases using the Arrhenius definition.

Examples of both types of acids and bases are shown in **Table 1**.

---

[1] **Svante August Arrhenius** (1859 – 1927) was a Swedish scientist who was one of the founders of the science of physical chemistry. He received the Nobel Prize for Chemistry in 1903.

Strong Acids and Strong Bases

In aqueous solutions of **strong acids** and **strong bases**, essentially all of the dissolved acid or base molecules will dissociate into ions. Strong acids and bases are, by definition, strong electrolytes in water. This is shown below:

Dissociation of a generic strong acid: $HAnion_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Anion^-_{(aq)}$

Specific example: hydrochloric acid: $HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

Dissociation of a generic strong base: $CationOH_{(aq)} + H_2O_{(l)} \rightarrow Cation^+_{(aq)} + OH^-_{(aq)}$

Specific example: sodium hydroxide: $NaOH_{(aq)} + H_2O_{(l)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

The right arrow implies that these reactions essentially go to completion, so very few of the intact acid HCl molecules or base NaOH molecules remain in solution.[2]

Table 1. Examples of Arrhenius and Brønsted-Lowry acids and bases.

Arrhenius Acid (forms H_3O^+ in water)	**Arrhenius Base** (forms OH^- in water)
$\mathbf{HCl_{(aq)} + H_2O \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}}$ hydrochloric acid $\mathbf{HCOOH_{(aq)} + H_2O \rightarrow H_3O^+_{(aq)} + HCOO^-_{(aq)}}$ formic acid formate anion	$\mathbf{NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}}$ sodium hydroxide
Brønsted-Lowry Acid (donates H^+, forms H_3O^+ in water)	**Brønsted-Lowry Base** (accepts H^+)
Same as above	$\mathbf{HCOO^-_{(aq)} + H^+_{(aq)} \rightarrow HCOOH_{(aq)}}$ formate anion formic acid $\mathbf{NH_{3(aq)} + H^+_{(aq)} \rightarrow NH_4^+_{(aq)}}$ ammonia ammonium cation

---

[2] Most bases, like NaOH, are really ionic solids with repeating Cation-OH units. An exception is ammonia, NH_3, which is truly a molecule with covalent bonds.

The concentration of the ions formed from a strong acid or strong base can be determined by the stoichiometric relationship of the original acid or base to its dissociated ions. In the case of both HCl and NaOH, the concentration of each dissociated ion is equal to the concentration of the original molecule. In other words, for the bottle of HCl shown in **Figure 1**, even though the label reads 0.10 M HCl, there are almost no intact HCl molecules in the bottle. Rather, it has dissociated into 0.10 M H^+ ions and 0.10 M Cl^- ions. Similarly, a bottle of 0.10 M NaOH contains 0.10 M Na^+ ions and 0.10 M OH^- ions.

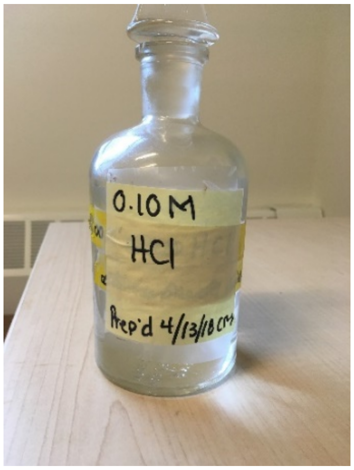

Figure 1. A bottle of 0.10 M hydrochloric acid.

A Note about Notation: Hydronium ions are represented here as $\mathbf{H_3O^+}$ (aq) to illustrate the fact that protons are donated from an acid to a water molecule. There are no free protons wandering about in aqueous solutions. Nonetheless, chemists often use the shorthand $\mathbf{H^+}$ to represent hydronium ions. They are synonymous.

Weak Acids and Weak Bases

In aqueous solutions of weak acids and weak bases, a small fraction of the dissolved acid or base molecules will react with water to form ions. Most of the molecules of weak acid or weak base retain their original structure. Weak acids and weak bases are weak electrolytes in aqueous solution. In addition, the ions that do form when weak acids or weak bases react with water will regenerate the original weak acid or weak base. This is an example of a **dynamic chemical equilibrium**, designated by **reversible arrows** ($\rightleftharpoons$). The anion formed when the acid dissociates is the **conjugate base** because it can accept a proton (H^+) to form the original acid. Similarly, the cation formed when the base accepts a proton from water is the **conjugate acid** because it can lose a proton to re-form the original base. Examples of weak acid and weak base equilibria are shown below.

Equilibrium of a generic weak acid: $HAnion_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Anion_{(aq)}$

e.g. formic acid $HCOOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCOO^-_{(aq)}$

Equilibrium of a generic weak base: $Base_{(aq)} + H_2O_{(l)} \rightleftharpoons BaseH^+_{(aq)} + OH^-_{(aq)}$

e.g. ammonia $NH_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$

The equilibrium reversible arrow implies that species on both sides of the arrow are present in solution. This is not the case for strong acid and strong base equilibria, in which the concentrations of products are much higher than reactants.

Weak Acid and Weak Base Equilibrium

Chemical species in dynamic equilibrium are governed by a value known as the equilibrium constant. For the equilibrium of a generic weak acid shown above, the concentrations of all the species are related by an equilibrium constant (K_{eq}), **Equation 1**. The equilibrium constant of a weak acid is called an “acidity constant” and is denoted K_a.

$$K_{eq} \text{ of a weak acid} = K_a = \frac{[H_3O^+][\text{Anion}]}{[\text{HAnion}]} = \frac{[H_3O^+][\text{conjugate base}]}{[\text{acid}]} \qquad \textbf{(Equation 1)}$$

The concentration of liquid water does not appear in the expression because it is assumed to be a constant and is included in the equilibrium constant. Equilibrium of a weak base is governed by the "basicity constant", K_b, as shown in **Equation 2**.

$$K_{eq} \text{ of a weak base} = K_b = \frac{[\text{BaseH}^+][\text{OH}^-]}{[\text{base}]} = \frac{[\text{conjugate acid}][\text{OH}^-]}{[\text{base}]} \quad \textbf{(Equation 2)}$$

The magnitude of the equilibrium constant signifies the extent to which the chemical reaction will proceed forward to achieve equilibrium. A large K_{eq} indicates that equilibrium lies to the right, so products are favored over reactant at equilibrium; a small K_{eq} means that the equilibrium lies to the left, so reactants are favored over product at equilibrium. The chemical equilibria and equilibrium constants of several weak acids and weak bases are listed in **Table 2**. Note two properties of the K_{eq} values:

1. They are always positive ($K_{eq} > 0$), and
2. They are typically very small ($K_{eq} << 1$), as indicated by the **negative powers of ten** (e.g. 4.2×10^{-7} for carbonic acid)

Table 2. Equilibrium constants for some common weak acids and bases. Source: *CRC Handbook of Chemistry and Physics, 2009/2010 (90th ed.)*

Weak Acids	**Chemical Formula**	**Chemical Equilibrium**	**K_a**
Formic acid	H_2CO_2	$H_2COO^-_{(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + HCOO^-_{(aq)}$	1.8×10^{-4}
Acetic acid	$HC_2H_3O_2$	$HC_2H_3O_{2(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + C_2H_3O_2{}^-_{(aq)}$	1.75×10^{-5}
Propionic acid	$HC_3H_5O_2$	$HC_3H_5O_{2\,(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + C_3H_5O_2{}^-_{(aq)}$	1.5×10^{-5}
Carbonic acid	H_2CO_3	$H_2CO_{3(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + HCO_3{}^-_{(aq)}$	4.5×10^{-7}
Bicarbonate ion	$HCO_3{}^-$	$HCO_3{}^-_{(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + CO_3{}^{2-}_{(aq)}$	4.7×10^{-11}
Hypochlorous acid	$HClO$	$HClO_{(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + ClO^-_{(aq)}$	4.0×10^{-8}
Nitrous acid	HNO_2	$HNO_{2(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + NO_2{}^-_{(aq)}$	5.6×10^{-4}
Ammonium ion	$NH_4{}^+$	$NH_4{}^+_{(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + NH_{3(aq)}$	5.6×10^{-10}
Hydrogen cyanide	HCN	$HCN_{(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + CN^-_{(aq)}$	6.2×10^{-10}
Weak Bases	**Chemical Formula**	**Chemical Equilibrium**	**K_b**
Carbonate ion	$CO_3{}^{2-}$	$CO_3{}^{2-}_{(aq)} + H_2O_{(l)} \leftrightharpoons HCO_3{}^-_{(aq)} + OH^-_{(aq)}$	2.14×10^{-4}
Bicarbonate ion	$HCO_3{}^-$	$HCO_3{}^-_{(aq)} + H_2O_{(l)} \leftrightharpoons H_2CO_{3(aq)} + OH^-_{(aq)}$	2.24×10^{-8}
Cyanide ion	CN^-	$CN^-_{(aq)} + H_2O_{(l)} \leftrightharpoons HCN_{(aq)} + OH^-_{(aq)}$	1.6×10^{-5}
Ammonia	NH_3	$NH_{3(aq)} + H_2O_{(l)} \leftrightharpoons NH_4{}^+_{(aq)} + OH^-_{(aq)}$	1.8×10^{-5}

Part B. Water, and the pH and pOH scales

The Auto-Ionization of Water

In the above equilibrium expression, the concentrations of the hydronium ion and hydroxide play an important role. These species are inter-related. Liquid water dissociates, or auto-ionizes, to a small extent according to **Equation 3.**

$$2H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + OH^-_{(aq)} \qquad \textbf{(Equation 3)}$$

The equilibrium expression for this reaction is shown in **Equation 4**.

$$K_{eq} = K_w = [H_3O^+][OH^-] \qquad \textbf{(Equation 4)}$$

The equilibrium constant for this reaction is the **dissociation constant** for water, denoted K_w. At 25°C, $K_w = 1.00 \times 10^{-14}$. K_w varies somewhat as temperature changes.

Equation 4 shows that the product of the hydronium and hydroxide concentrations is a constant (K_w). It also shows that in neutral water, the concentrations of hydronium and hydroxide ions are equal because they are formed in a 1:1 ratio (see **Equation 3**). In other words, in pure water, $[H_3O^+] = [OH^-]$. Substituting this information into **Equation 4**, we can derive the molar concentration of each ion in pure water, as shown below:

$$[H_3O^+][OH^-] = 1.00 \times 10^{-14}$$
$$[H_3O^+]^2 = 1.00 \times 10^{-14}$$
$$[H_3O^+] = 1.00 \times 10^{-7}$$

and thus, $[OH^-] = 1.00 \times 10^{-7}$, assuming T = 25ºC.

This establishes a reference point. In pure[3] water, the concentration of hydronium and hydroxide ions is 10^{-7} mol/L. Since there are 55.5 moles of water in a liter under standard conditions, this means that fewer than **two** out of **one billion** water molecules are dissociated. That's right, just two.

When an acid is dissolved in water, $[H_3O^+]$ increases and $[OH^-]$ decreases, making the solution acidic. Conversely, when a base is dissolved in water, $[H_3O^+]$ decreases and $[OH^-]$ increases, making the solution basic. This is universally true, regardless of the species of acid or base.

Furthermore, K_w equals the product of the acidity and basicity constants for any acid and its conjugate base, as shown in **Equation 5.** The stronger an acid (and the larger its K_a), the weaker its conjugate base (the smaller its K_b value); the product must equal 1.00×10^{-14}.

$$K_a \bullet K_b = K_w \qquad \textbf{(Equation 5)}$$

---

[3] Due to its ability to dissolve so many substances, absolutely pure water is hard to come by. Tap water contains dissolved minerals, gases (air), and added chemicals (e.g. chlorine as a disinfectant). De-ionized water is almost free of ions, but still contains dissolved gases.

The pH Scale

The molar concentration of H_3O^+ in aqueous solutions is a measure of its **acidity** or **alkalinity**. The more concentrated the hydronium ion, the more acidic the solution. The pH is defined as the negative log of $[H_3O^+]$ as shown in **Equation 6.**

$$\mathrm{pH} = -\log\,[H_3O^+] \qquad \textbf{(Equation 6)}$$

To convert pH to $[H_3O^+]$, the anti-log is taken as shown in **Equation 7**.

$$[H_3O^+] = 10^{-\mathrm{pH}} \qquad \textbf{(Equation 7)}$$

The pH scale, shown in **Figure 2**, commonly spans a range of 0 – 14. A neutral solution is defined by a pH value of 7. Acidic values are defined as pH < 7, and alkaline (or basic) values are defined as pH > 7. Representative pH values are shown in the figure. In your body, stomach digestive juices are quite acidic, with a pH~2. In contrast, intestinal fluid is somewhat alkaline, with a pH of ~8. Note that aqueous solutions with pH values below 0 (i.e. negative numbers) and above 14 are possible. For example, the theoretical pH of a 5 M solution of HCl is:

$$\mathrm{pH} = -\log[5] = -0.7$$

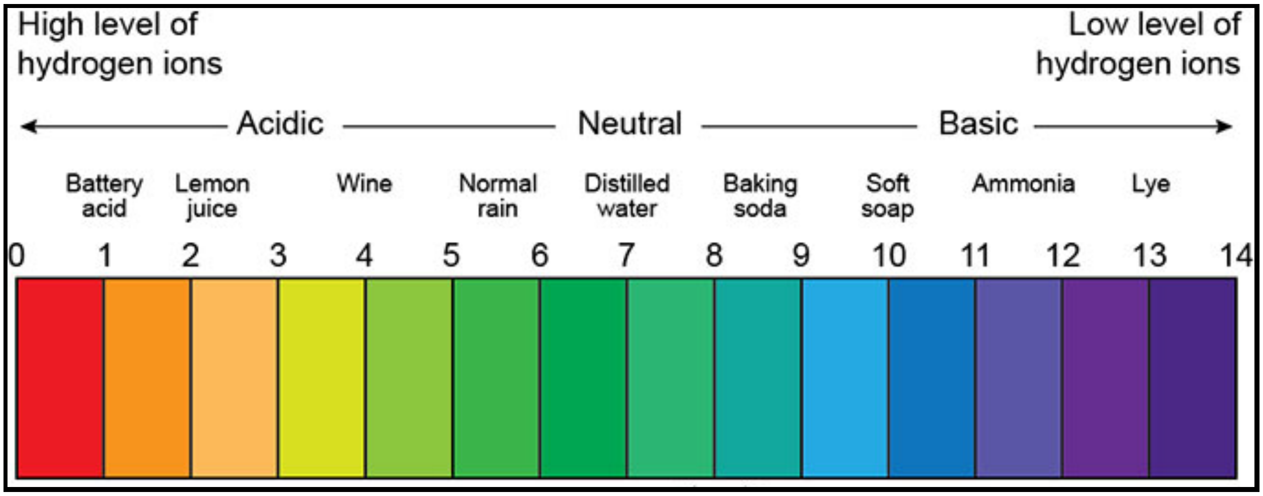

Figure 2. The pH scale. The concentration of H_3O^+ decreases by a factor of 10 for every unit increase in pH. *Source: Queen Mary University of London* https://www.qmul.ac.uk/chesswatch/water-quality-sensors/ph/

The pOH Scale

The degree of alkalinity of a solution may be expressed by **pOH**, which is a measure of the molar concentration of OH^- ions. This is analogous to the relationship between pH and the H_3O^+ ion concentration and is expressed in **Equations 8** and **9**.

$$\mathrm{pOH} = -\log[OH^-] \qquad \textbf{(Equation 8)}$$

$$[OH^-] = 10^{-\mathrm{pOH}} \qquad \textbf{(Equation 9)}$$

When $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M in neutral solution, then pH = pOH = 7.

Mathematically, if A x B = C, then log (A) + log (B) = log (C). Therefore,

$$\text{pH} + \text{pOH} = -\log K_w = 14.0 \qquad \text{at } 25°\text{C} \qquad \textbf{(Equation 10)}$$

The pH of Salt Solutions

Salts are ionic compounds composed of positively charged cations and negatively charged anions. When soluble ionic compounds dissolve in water, the ions separate and are surrounded by a sphere of water molecules called a **hydration shell**.

In some cases, ions from the original salt will react with the surrounding water, resulting in the breakage of one of the covalent bonds in the water molecule. This type of chemical reaction is called **hydrolysis**. Two types of hydrolysis are possible, written generically as:

$$\text{Cation}^+ + 2H_2O \rightleftarrows \text{CationOH} + H_3O^+$$

and

$$\text{Anion}^- + H_2O \rightleftarrows \text{HAnion} + OH^-$$

The extent to which these equilibrium reactions occur is governed by the stability of the products. The stability of the products depends on whether the CationOH (a base) or HAnion (an acid) is **strong** or **weak**. If it is a strong base or strong acid, then it will exist as dissociated ions; the hydrolysis reaction will form almost no products. The base exists as Cation^+ and the acid as Anion^-.

In contrast, a weak acid or weak base will exist in both the dissociated and un-dissociated forms. Three examples are given below.

Example 1: Dissolving sodium chloride in water.

When NaCl dissolves, it dissociates completely: $NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$

Hydrolysis of the cation is written as:

$$Na^+_{(aq)} + 2H_2O_{(l)} \leftrightharpoons NaOH_{(aq)} + H_3O^+_{(aq)}$$

This is an equilibrium reaction, but NaOH is a strong base and so the equilibrium lies far to the left. There is so little NaOH in solution that we can say **the forward reaction is negligible.**

Hydrolysis of the anion is written as:

$$Cl^-_{(aq)} + H_2O_{(l)} \leftrightharpoons HCl_{(aq)} + OH^-_{(aq)}$$

HCl is a strong acid so, as with NaOH, the equilibrium lies far to the left. Again, **the forward reaction is negligible**. Since both forward reactions are negligible, there is **no net hydrolysis** and the solution is **neutral (pH ~ 7)**.

In contrast, consider a salt where the cation is too weak to react with water, but the anion reacts with water to form a weak acid and hydroxide. The anion undergoes hydrolysis, whereas the cation does not. The resulting solution will be basic (pH > 7), so the salt is considered a **basic salt**.

Example 2: Dissolving sodium hypochlorite[4] in water

$$NaClO(s) + H_2O\ (l) \rightarrow Na^+\ (aq) + ClO^-\ (aq)$$

As in the first example, hydrolysis of the cation is written as:

$$Na^+_{(aq)} + 2H_2O_{(l)} \leftrightharpoons NaOH_{\ (aq)} + H_3O^+_{(aq)}$$

NaOH is a strong base, making the forward reaction negligible.

Hydrolysis of the anion is written as:

$$ClO^-\ (aq) + H_2O\ (l) \leftrightharpoons HClO\ (aq) + OH^-\ (aq)$$

HClO is a **weak acid** so most of what is formed will remain intact; both the forward and backward reactions are significant. Significant amounts of both HClO and OH^- will remain in solution. Since the above occurs to an appreciable extent, there is **a net hydrolysis** and the solution is **basic (pH > 7)**.

We can divide soluble salts into four categories depending on whether the cation, anion, or both, undergo hydrolysis. These categories are described in **Table 3**. Categories 1 – 3 are well defined: the resulting solution is neutral, basic, or acidic. For category 4, both ions undergo hydrolysis. To estimate the pH of the resulting solution, you must compare the relevant K_a and K_b values. The larger equilibrium constant indicates which equilibrium (weak acid or weak base) occurs to a greater extent. This in turn tells you whether the salt will form an acidic or basic solution.

If K_a of the cation > K_b of the anion, the resulting solution is acidic.

If K_b of the anion > K_a of the cation, the resulting solution is basic.

The difference between K_a and K_b determines how acidic or basic the solution is. If the two K values are equal, then the two equilibria occur to the same extent and there is no net hydrolysis. The salt forms a neutral solution.

---

[4] Sodium hypochlorite is common household bleach.

Table 3. Types of salts and the characteristics for their aqueous solutions.

Type	pH	Characteristics	Examples
Neutral	~ 7	Cation is the conjugate of a strong base: too weak to react with water Anion is the conjugate of a strong acid: too weak to react with water **Neither ion undergoes hydrolysis.**	NaCl KBr KNO_3
Basic	> 7	Cation is the conjugate of a strong base: too weak to react with water Anion is the conjugate of a weak acid: it is a weak base **Anion undergoes hydrolysis, forming OH^-.**	NaClO $KC_2H_3O_2$ $KC_4H_7O_2$
Acidic	< 7	Cation is the conjugate of a weak base: it is a weak acid Anion is the conjugate of a strong acid: too weak to react with water **Cation undergoes hydrolysis, forming H_3O^+.**	NH_4Cl $Fe(NO_3)_3$
Acidic, Basic, or Neutral	See Note*	Cation is the conjugate of a weak base: it is a weak acid Anion is the conjugate of a weak acid: it is a weak base **Both ions undergo hydrolysis, forming both OH^- and H_3O^+.**	NH_4ClO $NH_4C_2H_3O_2$

* To estimate the pH of a salt solution, compare the values of the K_b for the anion (which acts as a base) with the K_a for the cation (which acts as an acid) to see which is stronger. This determines whether more OH^- or H_3O^+ is formed.

Example 3: **Dissolving ammonium hypochlorite, NH_4ClO, in water.**

To determine the relative pH of this salt solution, we must compare the values of K_b for the anion (the base) with the K_a for the cation (the acid).

Cation hydrolysis: $NH_4^+ (aq) + H_2O (l) \rightarrow H_3O^+ (aq) + NH_3 (aq)$ $K_a = 5.6 \times 10^{-10}$

Anion hydrolysis: $ClO^- (aq) + H_2O (l) \rightarrow OH^- + HClO (aq)$ $K_b = ??$

To determine the K_b for the anion, we can look up the K_a for conjugate acid, HClO.

$$HClO_{(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + ClO^-_{(aq)} \qquad K_a = 3.0 \times 10^{-8}$$

Now rearrange **Equation 5** to solve for K_b:

$$K_b = K_w/K_a = (1.0 \times 10^{-14})/(3.0 \times 10^{-8}) = 3.3 \times 10^{-7}$$

K_b for the hypochlorite anion, 3.3×10^{-7}, is far greater than K_a for the ammonium cation, 5.6×10^{-10}. Therefore the hydrolysis of the weak base occurs to a greater extent than the hydrolysis of the weak acid, generating more OH^- than H_3O^+ and **the resulting solution is basic**.

Part C. Calculating pH, pOH, and K_a: Examples

A. Strong Acid: Calculate the pH and pOH of a 0.15 M solution of nitric acid (HNO_3).

We may assume that all of the strong acid molecules dissociate. Using **Equation 6** we can calculate the pH directly from the concentration of $[H_3O^+]$. The concentration $[HNO_3]_{added}$ = 0.15 M, so

$$[H_3O^+] = [NO_3^-] = 0.15 \text{ M}$$

Now we can use the negative log to solve for pH:

$$pH = -\log [H_3O^+] = -\log (0.15) = 0.82$$

pOH may be calculated by rearranging **Equation 10**: $pOH = -\log K_w - pH$. Assuming standard conditions (25°C), we have

$$pOH = 14.0 - pH$$

$$pOH = 14.0 - 0.82 = 13.18$$

B. Weak Acid: Calculate the pH of a 0.15 M solution of hypochlorous acid, HClO, a weak acid.

Recall that weak acids only partially hydrolyze. In this case, hypochlorous acid partially reacts with water and is expressed in the following reversible chemical equilibrium:

$$HClO_{(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + ClO^-_{(aq)}$$

We can write an equilibrium expression for this reaction (see generic version in **Equation 1)**, using the K_a from **Table 2** for hypochlorous acid:

$$K_a = 3.0 \times 10^{-8} = \frac{[H_3O^+][ClO^-]}{[HClO]}$$

where $[H_3O^+]$, $[ClO^-]$, and $[HClO]$ are the equilibrium concentrations in mol/L.

We can assume that all of the hydronium and ClO^- ions are supplied by the dissociation of the weak acid. Thus, every dissociated molecule of HClO produces one H_3O^+ and one ClO^-. Therefore, $[H_3O^+] = [ClO^-]$. We can use this information to simplify the calculation as shown below:

$$K_a = 3.0 \times 10^{-8} = \frac{[H_3O^+]^2}{[HClO]}$$

What about the concentration of HClO? We know that the weak acid is *either* undissociated (HClO) *or* dissociated (ClO^-). Let's perform a mass balance. The initial concentration of the weak acid, $[HClO]_{initial,}$ is the amount (moles) of acid added, divided by the volume (L) of the solution. Doing a mass balance, we have:

$$[HClO]_{initial} = [HClO] + [ClO^-] \qquad \textbf{(Equation 11)}$$

The question before us: to what extent does the weak acid dissociate? To answer this, consider if the acid concentration is relatively high, compared to the K_a. When the concentration of the weak acid added is relatively high ($\frac{[acid]_{initial}}{K_a}$>400), we may assume that **an insignificant amount of the weak acid has dissociated.** In this example,

$$\frac{[acid]_{initial}}{K_a} = \frac{0.15}{3.0 \times 10^{-8}} = 5.0 \times 10^6.$$

Therefore, we may assume here that very little HClO has dissociated. Thus, [HClO] ~0.15M. Using this assumption, the K_a expression becomes:

$$K_a = 3.0 \times 10^{-8} = \frac{[H_3O^+]^2}{0.15}$$

We can now solve for $[H_3O^+]$:

$$[H_3O^+]^2 = 0.15 \text{ x } (3.0 \text{ x } 10^{-8}) = 4.5 \text{ x } 10^{-9}$$

By taking the square root, we get:

$$[H_3O^+] = 6.7 \text{ x } 10^{-5}$$

Using the negative log to solve for pH:

$$pH = -\log[H_3O^+] = -\log(6.7 \text{ x } 10^{-5}) = 4.17$$

Clearly, HClO is a much weaker acid than HNO_3. This is seen by comparing the pH of solutions of identical acid concentrations:

0.15 M HClO has **pH=4.17**, while

0.15 M HNO_3 has **pH=0.82**

Above we assumed that very little of the weak acid dissociates, but this is only true in more concentrated solutions. As molarity drops, it becomes less and less true. To determine the pH of low concentrations of weak acids, where $\frac{[acid]_{initial}}{K_a}$<400, we must make use of the quadratic formula:

$$[H_3O^+] = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad \textbf{(Equation 12)}$$

where

$a = 1$; $b = K_a$; $c = -K_a \bullet [acid]_{initial}$

This calculation should be used to calculate the pH of dilute solutions of a weak acid (Table 2B.)

C. Calculating K_a from measured pH.

In today's lab you will be measuring pH and calculating the K_a of a weak acid. Consider a generic weak acid, HA, which dissociates in water:

$$HA_{(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + A^-_{(aq)}$$

The acidity constant, as expressed in **Equation 1**, is:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad \textbf{(Equation 1)}$$

Performing a mass balance, as in **Equation 11,** we have:

$$[HA]_{initial} = [HA] + [A^-]$$

So the concentration of ***undissociated acid***, HA, is

$$[HA] = [HA]_{initial} - [A^-] \qquad \textbf{(Equation 13)}$$

Recall that for every dissociated molecule of HA we produce one H_3O^+ and one A^-. Therefore, $[H_3O^+] = [A^-]$. If we let x = $[H_3O^+]$, then:

$$K_a = \frac{x^2}{[HA]_{\text{initial}} - x} \qquad \textbf{(Equation 14)}$$

Recall that **Eq. 7** provides the means to calculate $x = [H_3O^+]$ from the pH.

Key Equations

1. K_{eq} of a weak acid

$$K_a = \frac{[H_3O^+][\text{Anion}]}{[\text{HAnion}]}$$

2. K_{eq} of a weak base

$$K_b = \frac{[\text{BaseH}^+][OH^-]}{[\text{base}]} = \frac{[\text{conjugate acid}][OH^-]}{[\text{base}]}$$

3. Dissociation constant for water

$$K_w = [H_3O^+][OH^-] \qquad \text{at } 25°\text{C}, K_w = 1.00 \text{ x } 10^{-14}.$$

4. pH, pOH scales

$$pH = -\log [H_3O^+] \qquad [H_3O^+] = 10^{-pH}$$
$$pOH = -\log [OH^-] \qquad [OH^-] = 10^{-pOH}$$

$$pH + pOH = -\log K_w = 14.0 \qquad \text{at } 25°\text{C}$$

5. Calculating theoretical pH:

Strong acid: $[H^+]$ = molarity of strong acid

Weak acid: $[H_3O^+] = \sqrt{([HA]_{initial} \text{ x } K_a)}$ when $\frac{[acid]_{initial}}{K_a} > 400$

use Equation 12 when $\frac{[acid]_{initial}}{K_a} < 400$

6. Calculating K_a from pH:

If we let $x = [H_3O^+]$, then:

$$K_a = \frac{x^2}{[HA]_{\text{initial}} - x}$$

Notes

Name ______________________________ No partner
Today's Date ____________ Section _____ Instructor ___________________________

Pre-Laboratory Assignment

Complete prelab questions prior to lab. Your instructor will let you know how to submit the pre-lab. All answers must be handwritten neatly.

1. Distinguish between the following terms:

   a. strong acid vs. strong base

   b. strong acid vs. weak acid

2. Complete the following calculations. But first...read the note about significant figures in Part D. Show all calculations.

   a. The pH when $[H_3O^+] = 1.5 \times 10^{-3}$ M.

   b. The pH when $[OH^-] = 3.1 \times 10^{-4}$ M.

   c. The $[H_3O^+]$ when pH = 8.42.

   d. The $[H_3O^+]$ when pOH = 5.58.

3. You may be surprised (but do not be overly concerned!) that the water from the sink is not pH 7.

   a. What body of water does Le Moyne's tap water come from? Look online for information about the City of Syracuse water supply.

      Provide the source of your information below. Give complete URL for on-line sources.

      ____

   b. Why might the pH of this water be anything other than 7? What other substances in the water might alter the pH? (Consider what is naturally present in the water, and what is added to the water.)

4. Complete the following table:

Salt	**Ions**	**Hydrolysis Reaction for Each Ion (If the hydrolysis reaction is negligible, write N/A)**	**Is the salt acidic, basic, or neutral?**
$NaC_2H_3O_2$			
NH_4Cl			
$NaHCO_3$			

Name ______________________________ No partner
Today's Date _____________ Section _____ Instructor ___________________________
CHM 152 Lab; Studying the pH of Acid, Base, and Salt Solutions, rev. January 26, 2021

Part D: In-Lab Portion

This procedure is provided for your information. This shows how the experimental pH data are generated.

Chemical Alert

0.10 M acetic acid (CH_3COOH)	**Mildly corrosive, irritant**
0.10 M hydrochloric acid (HCl)	**Corrosive, irritant**

Caution: Wear departmentally approved eye protection and gloves while performing this experiment. Prevent contact with eyes, skin, and clothing. Avoid inhaling vapors and ingesting the solutions.

Laboratory Materials

Reagents	**Reagents**	pH meter and probe
Buffer solutions (pH 4, 7, 10)	0.50 M sodium acetate	Medium test tubes (5)
0.10 M acetic acid	0.50 M sodium carbonate	10-mL graduated cylinder
0.10 M hydrochloric acid	0.50 M ammonium chloride	50-mL volumetric flask (3)
0.50 M sodium chloride	0.50 M ammonium acetate	5-mL volumetric pipet
		Pipet pump/bulb

Experimental Summary

Part I: Measure the pH of a strong acid (HCl) by preparing serial dilutions of the stock HCl solution. Calculate the theoretical pH of each solution and compare them to the measured pH.

Part II: Measure the pH of a weak acid (acetic acid) by preparing serial dilutions of the stock acetic acid solution. Calculate the theoretical pH of the each solution and compare to the measured pH. Calculate the experimental Ka value and compare to the known value.

Part III: Measure the pH of several salt solutions. Determine the expected pH range (acidic, basic, neutral) for each salt solution and compare it to the measured pH value.

Important

It is important that glassware is clean for this experiment. The presence of a contaminant will greatly affect the pH value you measure. Wash all glassware (except the volumetric pipet, flask and pH probe) with soap and warm tap water before beginning the lab. Finally, rinse the glassware with tap water, followed by DI water.

To clean the volumetric pipet, rinse the pipet with DI water and then rinse with the solution of interest. Do not use glassware soap to clean the pipet.

Similarly, rinse the volumetric flasks with tap water followed by DI water. Do not use glassware soap to clean the volumetric flask. If the flask is visibly stained, don't use it.

Calibrate the pH Meter and Probe

1. Using the three certified buffer solutions (4.01, 7.00, and 10.00), follow the instructions printed on the back of the pH meter to calibrate the probe and meter.

   Be sure to thoroughly rinse the probe with DI water over a waste beaker before using, and between buffer solutions. Gently shake the probe to remove excess water before placing the probe into the sample. Or use a clean KimWipe to remove excess water. **Do not** tap the probe against the beaker, as this may damage the probe.

   Be **extremely** careful to not damage the glass bulb of the pH probe. It is **extremely fragile and quite expensive.**

2. Once the pH meter is calibrated, it can be used to read the pH of each solution without recalibration. Always keep the pH electrode in a small amount of buffer solution to prevent the probe from drying out.

   The meter may "sleep" between readings. Unless you turn off the meter, you should not need to recalibrate it.

Part I: Preparing HCl Solutions by Serial Dilution and Determining pH

1. Label four medium test tubes "1 – 4".

Solution 1

2. Add ~ 10 mL of 0.10 M HCl to **Test Tube 1**.

Solution 2 (first dilution)

3. Label a **clean** 50-mL volumetric flask "**Soln 2**".

4. Pipet exactly 5.00 mL of 0.10 M HCl from Test Tube 1 into the 50-mL volumetric flask.

5. Carefully fill the 50-mL volumetric flask with DI water to the etched line.

6. Stopper and thoroughly mix the contents of the flask.

7. Transfer ~10 mL of **Solution 2** into **Test Tube 2.**

Solution 3 (second dilution)

8. Label a second, clean 50-mL volumetric flask "**Solution 3**".

9. Pipet exactly 5.00 mL of **Solution 2** from **Test Tube 2** into the **Solution 3** 50-mL volumetric flask.

10. Carefully fill the 50-mL volumetric flask with DI water to the etched line.

11. Stopper and thoroughly mix the contents of the flask.

12. Transfer ~10 mL of **Solution 3** into **Test Tube 3.**

Solution 4 (third dilution)

13. Label a second, clean 50-mL volumetric flask "**Solution 4**".

14. Pipet exactly 5.00 mL of **Solution 3** from **Test Tube 3** into the **Solution 4** 50-mL volumetric flask.

15. Carefully fill the 50-mL volumetric flask with DI water to the etched line.

16. Stopper and thoroughly mix the contents of the flask.

17. Transfer ~5 mL of **Solution 4** into **Test Tube 4.**

Measure the pH of each solution

18. Using the calibrated pH meter and probe, measure the pH of solutions 1 – 4 in the test tubes. Measure the **most dilute solution first (lowest acid concentration)**. Rinse the pH probe with DI water between measurements. Record the pH values on **Data Table 1**.

Part II: Preparing CH_3COOH (acetic acid) Solutions by Serial Dilution and Determining pH and K_a

Repeat **all** steps from **Part I** to prepare serial dilutions of acetic acid using 0.10 M acetic acid as **Solution 1**. Record the pH values on **Data Table 2A**. Copy the pH values again into **Data Table 2B**.

Part III: Predicting Hydrolysis of Various Salt Solutions

1. Obtain 5 clean medium test tubes and label A – E. The test tubes should be clean but do not have to be completely dry.

2. Place ~ 5 mL of the following solutions into their respective test tube:

    A. 0.50 M NaCl (sodium chloride)
    B. 0.50 M $NaC_2H_3O_2$ (sodium acetate)
    C. 0.50 M Na_2CO_3 (sodium carbonate)
    D. 0.50 M NH_4Cl (ammonium chloride)
    E. 0.50 M $NH_4C_2H_3O_2$ (ammonium acetate)

3. Using the calibrated pH meter and probe, measure the pH of each salt solution. Be sure to thoroughly clean the pH probe with DI water between each measurement. Record the pH values on **Data Table 3**.

<u>A note about significant figures:</u>

Logarithms and exponents distort significant figures in a significant way. A variation of ± 0.01 pH unit produces a 5% variation in $[H_3O^+]$. So, two significant figures in $[H_3O^+]$ translates into three significant figures in pH, and vice versa.

Bottom line: calculate pH to the 0.01 place. Report $[H_3O^+]$ to two significant figures.

Name ______________________________ No partner

Today's Date _____________ Section _____ Instructor ___________________________

CHM 152 Lab; Studying the pH of Acid, Base, and Salt Solutions, rev. January 26, 2021

Data Tables

Handwrite your answers neatly. Turn in all Data Tables and Post Lab Questions. Show all calculations below the data tables.

From Part I: Preparing HCl Solutions.

Data Table 1. Measured pH compared to theoretical pH of HCl solutions.

Concentration of HCl	**Measured pH SUPPLIED SEPARATELY**	**Calculated [H_3O^+] (based on measured pH)**	**Theoretical pH (based on the given concentration of HCl)**
1.0×10^{-1} M			
1.0×10^{-2} M			
1.0×10^{-3} M			
1.0×10^{-4} M			

Calculations for Data Table 1:

Name ________________________________ No partner
Today's Date ______________ Section _____ Instructor _____________________________
CHM 152 Lab; Studying the pH of Acid, Base, and Salt Solutions, rev. January 26, 2021

From Part II: CH_3COOH (acetic acid) Solutions

Data Table 2A. Measured pH, calculated $[H_3O^+]$ and acidity constant.

Concentration of CH_3COOH	**Measured pH SUPPLIED SEPARATELY**	**Calculated $[H_3O^+]$ (based on measured pH)**	**Calculated K_a (based on measured pH)**
1.0×10^{-1} M			
1.0×10^{-2} M			
1.0×10^{-3} M			
1.0×10^{-4} M			

Calculations for Data Table 2A:

Name ______________________________ No partner
Today's Date _____________ Section _____ Instructor ___________________________

From Part II: CH_3COOH (acetic acid) Solutions

Table 2B. Measured pH and calculated (theoretical) pH based on literature $K_a = 1.8 \times 10^{-5}$

Initial Concentration of CH_3COOH	Measured pH (same as Table 2A)	Theoretical $[H_3O^+]$	Theoretical pH
1.0×10^{-1} M			
1.0×10^{-2} M			
1.0×10^{-3} M			*
1.0×10^{-4} M			*

*** Use the quadratic equation for calculating $[H_3O^+]$ in the 1.0×10^{-3} M and 1.0×10^{-4} M acetic acid.**

Calculations for Data Table 2B:

Name ______________________________ No partner
Today's Date _____________ Section _____ Instructor ___________________________

CHM 152 Lab; Studying the pH of Acid, Base, and Salt Solutions, rev. January 26, 2021

Name ______________________________ No partner
Today's Date ____________ Section _____ Instructor __________________________

From Part III: Predicting Hydrolysis of Various Salt Solutions

Record the measured pH for each of the following five salt solutions in the appropriate box. Then, write any significant hydrolysis reactions for each ion in the salt. **If the hydrolysis reaction is negligible, write N/A.** The first one is already filled in for you.

The **significant reaction(s)** control the pH. From those reactions, predict how acidic or basic the solutions are expected to be: circle VA, SA, N, SB or VB in the appropriate box. Finally, circle whether or not your measured pH matches your predicted acidity/basicity.

VA = very acidic **SA** = slightly acidic **N** = neutral **SB** = slightly basic **VB** = very basic

Data Table 3. Hydrolysis reactions of salts.

NaCl	**Hydrolysis Reaction for Cation:**	**N/A**	
	Hydrolysis Reaction for Anion:		
	Predicted acidity/basicity: **VA SA N SB VB**	**Measured pH:**	**Match Prediction? Y N**
$NaC_2H_3O_2$	**Hydrolysis Reaction for Cation:**		
	Hydrolysis Reaction for Anion:		
	Predicted acidity/basicity: **VA SA N SB VB**	**Measured pH:**	**Match Prediction? Y N**
Na_2CO_3	**Hydrolysis Reaction for Cation:**		
	Hydrolysis Reaction for Anion:		
	Predicted acidity/basicity: **VA SA N SB VB**	**Measured pH:**	**Match Prediction? Y N**
NH_4Cl	**Hydrolysis Reaction for Cation:**		
	Hydrolysis Reaction for Anion:		
	Predicted acidity/basicity: **VA SA N SB VB**	**Measured pH:**	**Match Prediction? Y N**
$NH_4C_2H_3O_2$	**Hydrolysis Reaction for Cation:**		
	Hydrolysis Reaction for Anion:		
	Predicted acidity/basicity: **VA SA N SB VB**	**Measured pH:**	**Match Prediction? Y N**

Name ______________________________ No partner
Today's Date _____________ Section _____ Instructor ___________________________
CHM 152 Lab; Studying the pH of Acid, Base, and Salt Solutions, rev. January 26, 2021

Post Lab Questions

You will be calculating the K_a for the ammonium cation in two ways, one based on experimental data, and one based on known (published) values.

1. Using your data from Table 3 for 0.50 M NH_4Cl, calculate K_a for the ammonium ion using the measured pH of the salt solution.

2. For comparison, calculate the K_a for the ammonium cation, using the published value K_b for ammonia = 1.8×10^{-5}.

3. Comment on the difference between the two K_a values above. Which is larger? By what multiplicative factor are the two K_a values different?