

ACIDS, BASES & EQUILIBRIUM

In this lab you will investigate some equilibrium properties of acids and bases. The acidity of a solution at 25° C can be expressed using the pH scale. Acidic solutions have pH values less than 7, basic solutions have pH values greater than 7, and neutral solutions have a pH value equal to 7 at 25°C. In this experiment, you will use a pH electrode to determine the pH values of several acids, bases and salts. Red cabbage juice will be added to observe the different colors produced based on pH. The pH values will be used to determine the equilibrium % ionization and hydrolysis for a set of weak acids and bases.

OBJECTIVES

In this experiment, you will:

- Gain experience using a pH probe.
- Gain more experience preparing solutions of specified concentration.
- Be able to classify acids and bases as strong or weak.
- Recognize most salts are not neutral but give acidic or basic solutions when dissolved in water.
- Experimentally determine the % ionization and the equilibrium constant, K_a , of a weak acid.
- Experimentally determine the % hydrolysis and the equilibrium constant, K_b , of a weak base.
- Investigate the effect of initial solution concentration on percent ionization of a weak acid.

THE PH SCALE

In aqueous solutions, the concentration of the hydrogen ion, H^+ , (or more correctly the hydronium ion, H_3O^+) can vary over many orders of magnitude, 10 M to 10^{-15} M. The pH scale was developed to more conveniently handle this large range of concentration values. pH is the negative (base ten) logarithm of $[H_3O^+]$

$$pH = -\log_{10}[H_3O^+] \quad (1)$$

A 10^{-12} M H^+ solution has a pH of 12: $-\log(10^{-12}) = -(-12) = 12$. A 5.4×10^{-4} M H^+ solution has a pH of 3.27. Notice the lower the pH, the higher the $[H_3O^+]$. From equation (1) the concentration of hydrogen ions in solution can be found if the pH is known:

$$[H_3O^+] = 10^{-pH} \quad (2)$$

A pH of 6.25 gives a $[H_3O^+]$ of $10^{-6.25} = 5.6 \times 10^{-7}$ M.

The terms acidic and basic are relative designations and depend on the $[H_3O^+]$ at 25° C:

- Acidic: $[H_3O^+] > 1 \times 10^{-7}$ M, $pH < 7$
- Basic: $[H_3O^+] < 1 \times 10^{-7}$ M, $pH > 7$
- Neutral: $[H_3O^+] = 1 \times 10^{-7}$ M, $pH = 7$

The value of 7 for a neutral solution is not arbitrary but is derived from the equilibrium that exists in aqueous solutions between the hydrogen ion, $[H_3O^+]$, and the hydroxide ion concentrations, $[OH^-]$, at 25° C:



where K_w is the equilibrium constant. Since all equilibrium constants are temperature dependent, a better definition of a neutral solution is one where $[H_3O^+] = [OH^-]$. At 25° C a neutral solution has $[H_3O^+] = [OH^-] = 10^{-7}$, $pH = 7$, since $K_w = 10^{-14}$. You should be able to verify these concentrations by using equation 3. Since this equilibrium between $[H_3O^+]$ and $[OH^-]$ is constantly maintained in all aqueous solutions, from equation (3), as the $[H_3O^+]$ increases the $[OH^-]$ must decrease to reestablish the equilibrium. Thus, in acidic solutions, $[H_3O^+] > [OH^-]$. The opposite is true for basic solutions, $[H_3O^+] < [OH^-]$. For example, the $[OH^-]$ in an acidic solution that has a $[H_3O^+]$ of 3.4×10^{-4} M ($pH = 3.47$):

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{10^{-14}}{3.4 \times 10^{-4}} = 2.9 \times 10^{-11} \text{ M}$$

Like pH, pOH is defined for the hydroxide ion concentration as:

$$pOH = -\log_{10}[OH^-] \quad (4)$$

$$\text{and } [OH^-] = 10^{-pOH} \quad (5)$$

The relationship between pH and pOH at 25° C is easily derived by taking the $-\log()$ of equation 3:

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00 \quad (6)$$

In summary, knowledge of the any one of the four quantities: $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH, or pOH, at 25° C gives all the information needed to determine the remaining three quantities since the four values are related through the equations presented. For example, a solution has a pOH of 10.51. What is the $[\text{OH}^-]$, $[\text{H}_3\text{O}^+]$ and pH of the solution?

$$\begin{aligned} [\text{OH}^-] &= 10^{-\text{pOH}} = 10^{-10.51} = 3.1 \times 10^{-11} \\ [\text{H}_3\text{O}^+] &= \frac{K_w}{[\text{OH}^-]} = \frac{10^{-14}}{3.1 \times 10^{-11}} = 3.2 \times 10^{-4} \text{ M} \\ \text{pH} &= -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}(3.2 \times 10^{-4} \text{ M}) = 3.49 \end{aligned}$$

CLASSIFICATION OF ACIDS AND BASES AS STRONG OR WEAK

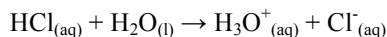
Common Strong Acids (**Memorize**): HCl, HBr, HI, HNO₃, HClO₃, HClO₄, H₂SO₄
Weak Acids – all other acids besides the seven common strong acids are considered weak,

Common Strong Bases (**Memorize**): LiOH, NaOH, KOH, RbOH, CsOH (Group 1A(1) metal hydroxides)
Ca(OH)₂, Sr(OH)₂, Ba(OH)₂ (Heavy Group 2A(2) metal hydroxides)

Weak Bases – all other bases especially ammonia and the amines, -NH₂.

STRONG ACID IONIZATION

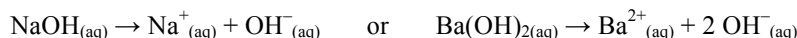
Strong acids IONIZE 100% in water. As a result, **aqueous strong acids only exist in the fully ionized form**. For a general strong acid such as HCl(aq) we write the IONIZATION equation as:



For sulfuric acid only one proton is fully ionized in solution: $\text{H}_2\text{SO}_{4(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{H}_3\text{O}^+_{(\text{aq})} + \text{HSO}_4^-_{(\text{aq})}$

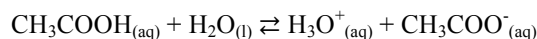
STRONG BASE DISSOCIATION

Strong bases DISSOCIATE 100% in water. As a result, **aqueous strong bases only exist in the fully ionized form**. NaOH(aq) and Ba(OH)₂(aq) we write the DISSOCIATION equation as:



WEAK ACID IONIZATION, THE K_a EQUILIBRIUM

Weak acids IONIZE a few percent (or less) in water. As a result equilibrium is established between the molecular and ionized forms. For example, one acid used in this experiment is acetic acid. The acetate ion produced in the ionization, CH_3COO^- , is defined as the CONJUGATE BASE of acetic acid.



The equilibrium expression, K_a , for the ionization is written as

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.75 \times 10^{-5} \text{ at } 25^\circ \text{ C} \quad (7)$$

The experimental K_a for acetic acid¹ is 1.75×10^{-5} at 25° C.

The greater the value of K_a the “stronger” is the weak acid. Weak acids can also be ranked by strength using $\text{p}K_a$ values:

$$\text{p}K_a = -\log_{10}(K_a) \quad (8)$$

The $\text{p}K_a$ of acetic acid is 4.756. The “stronger” the weak acid the smaller the $\text{p}K_a$ value.

¹ Lange's Handbook of Chemistry, 14th ed. 1992.

Table I gives the K_a and pK_a of some common weak acids. They are ranked according to strength. Strongest first.

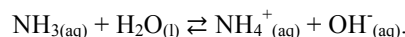
Table I. Some Common Weak Acids in Water at 25° C

Acid	Molecular Formula	Conjugate Base	K_a	pK_a
Hydrofluoric	HF	F ⁻	6.8×10^{-4}	3.17
Nitrous	HNO ₂	NO ₂ ⁻	4.5×10^{-4}	3.35
Benzoic	C ₆ H ₅ COOH	C ₆ H ₅ COO ⁻	6.5×10^{-5}	4.19
Acetic	CH ₃ COOH	CH ₃ COO ⁻	1.75×10^{-5}	4.756
Hypochlorous	HClO	ClO ⁻	3.0×10^{-8}	7.52
Hydrocyanic	HCN	CN ⁻	4.9×10^{-10}	9.31

WEAK BASE HYDROLYSIS, THE K_b EQUILIBRIUM

Weak bases HYDROLYZE a few percent (or less) in water. As a result equilibrium is established between the molecular and HYDROLYZED forms. In hydrolysis, one of the O-H bonds in water is broken and the hydrogen ion is transferred to the weak base producing its CONJUGATE ACID while leaving behind a hydroxide ion.

One weak base to be used in this experiment is ammonia, NH₃:



The ammonium ion, NH₄⁺, is the conjugate acid of ammonia. The K_b expression for the hydrolysis equilibrium is written as

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} \text{ at } 25^\circ \text{ C.} \quad (9)$$

Analogous to weak acids, for weak bases the larger the value of K_b the greater the % hydrolysis and consequently more hydroxide ions are produced at equilibrium. The greater the value of K_b the “stronger” is the weak base. Weak bases can also be ranked by strength using pK_b values:

$$pK_b = -\log(K_b) \quad (10)$$

The pK_b of ammonia is 4.74. The “stronger” the weak base the smaller the pK_b value.

% IONIZATION OF A WEAK ACID AND % HYDROLYSIS OF A WEAK BASE, ICE TABLES

The % ionization/hydrolysis for a weak acid/base is determined by the magnitude of K_a/K_b . Larger K values result in greater forward reaction and ionization or hydrolysis. We can define the % ionization/hydrolysis several ways, but the most useful way is through an ICE table. Consider a general weak acid, HA(aq.) and weak base, B(aq):

K_a	HA _(aq)	H ₂ O _(l)	\rightleftharpoons	H ₃ O ⁺ _(aq)	A ⁻ _(aq)
I	[HA] _i	—		1×10^{-7}	0
C	-x	—		+x	+x
E	[HA] _i - x	—		$1 \times 10^{-7} + x$	x

K_b	B _(aq)	H ₂ O _(l)	\rightleftharpoons	OH ⁻ _(aq)	BH ⁺ _(aq)
I	[B] _i	—		1×10^{-7}	0
C	-x	—		+x	+x
E	[B] _i - x	—		$1 \times 10^{-7} + x$	x

The acid % ionization and the base % hydrolysis are defined from the ICE tables as

$$\text{acid \% ionization} = \frac{x}{[\text{HA}]_i} \times 100\% \quad (11)$$

$$\text{and base \% hydrolysis} = \frac{x}{[\text{B}]_i} \times 100\% \quad (12)$$

K_a and K_b can also be defined in terms of x from the ICE table:

$$K_a = \frac{[1 \times 10^{-7} + x][x]}{[\text{HA}]_i - x} \approx \frac{x^2}{[\text{HA}]_i - x} \quad (13)$$

$$\text{and } K_b = \frac{[1 \times 10^{-7} + x][x]}{[B]_{i-x}} \approx \frac{x^2}{[B]_{i-x}} \quad (14)$$

USING PH MEASUREMENTS TO FIND % IONIZATION AND K_a

In this lab you will use pH measurements to calculate the % ionization and K_a for weak acids or the % hydrolysis and K_b for weak bases. Here is an example of calculation for a weak acid. Given a 0.10 M weak acid, HA(aq) has a measured pH of 2.26, calculate the % ionization and K_a for this weak acid.

1. Convert pH to $[H_3O^+]$: $[H_3O^+] = 10^{-pH} = 5.50 \times 10^{-3} \text{ M}$.
2. Find x in the ICE table: $[H_3O^+] = x + 1 \times 10^{-7} \text{ M}$; $x = [H_3O^+] - 1 \times 10^{-7} \text{ M} = 5.50 \times 10^{-3} \text{ M}$.
3. Calculate the % ionization: $\frac{x}{[HA]_i} \times 100\% = \frac{5.50 \times 10^{-3} \text{ M}}{0.10 \text{ M}} \times 100\% = 5.5\%$
4. Calculate the K_a : $\frac{[1 \times 10^{-7} + x][x]}{[HA]_{i-x}} \approx \frac{x^2}{[HA]_{i-x}} = \frac{(5.50 \times 10^{-3})^2}{(0.10 - 5.5 \times 10^{-3})} = 3.2 \times 10^{-4}$

Similar calculations are done using the pH of a weak base solution except we use the pH to find $[OH^-]$.

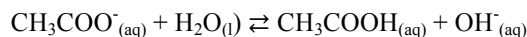
ACIDIC AND BASIC SALTS

Salts can also be classified according to their acid-base behavior. The acid-base behavior of salts comes from the possible interaction of the cations and anions with the water solvent. Many ions are able to react with water to generate H^+ or OH^- ions. A salt that contains a basic anion will be basic. A salt that contains an acidic cation will be acidic. A salt that contains neither a basic anion nor an acidic cation will be neutral. Examples salts are:

1. Sodium acetate, $NaCH_3COO$. The Na^+ ion is neutral. The CH_3COO^- ion is basic since it is the conjugate base of a weak acid. Sodium acetate is a basic salt and when dissolved in water will produce a basic solution.
2. Ammonium chloride, NH_4Cl . The NH_4^+ ion is acidic since it is the conjugate acid of a weak base. The Cl^- ion is neutral. Ammonium chloride is an acidic salt and when dissolved in water will produce an acidic solution.
3. Sodium chloride. Both ions are neutral. Sodium chloride is a neutral salt.

Basic Anions in Salts

Most anions in a soluble salt react with water (hydrolysis) to form OH^- ions and are thus **basic** anions. For example the acetate ion from sodium acetate is basic:



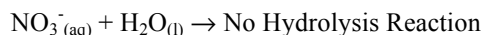
An equilibrium is established in water between the anion and the conjugate acid of the anion, acetic acid. As a result of this hydrolysis reaction, a solution of sodium acetate will be basic ($pH > 7$).

An equilibrium constant expression can be written for the acetate hydrolysis reaction and is given the symbol K_b , the same as any weak base since the reaction produces a basic solution:

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = 5.71 \times 10^{-10}$$

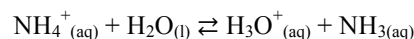
As always, K_b is calculated from equilibrium concentrations. K_b for the acetate ion is found to be 5.71×10^{-10} .

In contrast, anions that are the conjugate base of a strong acid, such as NO_3^- from HNO_3 , are not basic since no hydrolysis reaction takes place. The nitrate ion is much too weak a base to take a proton from water. The nitrate ion is therefore a NEUTRAL ion.



Acidic Cations in Salts

All cations except the group I and the heavier alkaline earth metals (Ca^{2+} , Sr^{2+} , and Ba^{2+}) act as weak acids in solution. It may surprise you that metal ions, such as Al^{3+} , and the transition metal ions form weakly acidic solutions. However, for this experiment we will be concerned with the ammonium ion, NH_4^+ . The ammonium ion reacts with water to produce hydronium ions:



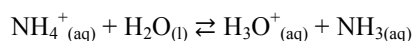
An equilibrium is established in water between the ammonium ion and ammonia. As a result of this ionization a solution of ammonium chloride will be acidic ($\text{pH} < 7$). An equilibrium constant expression can be written for the cation ionization and is given the symbol K_a since the cation acts as a weak acid towards water:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = 5.6 \times 10^{-10}$$

As always, equilibrium concentrations are used to calculate K_a . The accepted K_a for the ammonium ion is 5.6×10^{-10} .

Conjugate Acid-Base Pairs

When proton transfer occurs between reactants, we create a conjugate acid and conjugate base on the product side. For example



Here, $\text{NH}_4^+(\text{aq})$ is the reactant weak acid and the product $\text{NH}_3(\text{aq})$ is the *conjugate base* of $\text{NH}_4^+(\text{aq})$. At the same time, $\text{H}_2\text{O}(\text{l})$ is the reactant weak base and $\text{H}_3\text{O}^+(\text{aq})$ is the product *conjugate acid* of $\text{H}_2\text{O}(\text{l})$. $\text{NH}_4^+(\text{aq})$ and $\text{NH}_3(\text{aq})$ are said to be *conjugate acid-base pairs* while $\text{H}_3\text{O}^+(\text{aq})$ and $\text{H}_2\text{O}(\text{l})$ are also *conjugate acid-base pairs*. Every acid has a conjugate base, likewise every base has a conjugate acid. For *conjugate acid-base pairs* their K_a and K_b values are related through K_w : $K_a \times K_b = K_w$. (15)

MATERIALS

Equipment	Solutions	Acetic acid for dilution
LabQuest	0.10 M HCl	0.500 M acetic acid
Vernier pH Electrode	0.10 M NaOH	
wash bottle	0.10 M acetic acid	
stirring rod	0.10 M ammonia	
pH 4 and pH 10 Buffers	0.10 M ammonium chloride	
13+ large test tubes	0.10 M sodium carbonate	
test-tube rack	0.10 M sodium bicarbonate	
600-mL beaker	0.10 M sodium phosphate	
4 250-mL beakers	0.10 M sodium hydrogen phosphate	
50-mL beaker	0.10 M sodium dihydrogen phosphate	
100-mL graduated cylinder	Red cabbage juice indicator	
10-mL graduated cylinder		

PROCEDURE

Obtain and wear goggles. **CAUTION:** Do not eat or drink in the laboratory.

Part I Acid-base Solutions and Cabbage Juice Indicator

1. Obtain ≈ 5 mL of pH 4 buffer in a large, clean test tube. Obtain ≈ 5 mL of pH 10 buffer in a large, clean test tube. **You only need enough to cover the tip of the pH probe!** (Investigate the option of sharing buffer solutions with nearby groups.)
2. Prepare the pH probe for data collection with the LabQuest. Plug the pH probe into channel 1 on the LabQuest. **Select Choose Sensors ► Calibrate ► CH 1:pH.** From the calibrate menu **Select Calibrate Now.** Rinse the pH electrode and then immerse into one of the two buffer solutions. When the voltage stabilizes, enter the buffer pH into the LabQuest. **Select KEEP.** Repeat for the second buffer solution. **Select KEEP. Select OK.** The pH probe should be now be calibrated.
3. Measure ≈ 5 mL of each solution into separate test tubes. **CAUTION:** *Ammonia solution is toxic. Its liquid and vapor are extremely irritating, especially to eyes. Handle these solutions with care. Do not allow the solutions to contact your skin or clothing. Wear goggles at all times. Notify your teacher immediately in the event of an accident.*
4. Begin with the 0.10 M HCl solution. Immerse the pH electrode into the solution and slowly move the pH electrode up and down within the solution. **Note: readings may drift without proper movement of the electrode.** Record the measured pH reading from the display on your LabQuest in your notebook. **Record all pH readings to two decimal places only!** Rinse the pH probe between measurements.
5. Give this solution to your partner after measuring the pH. They can then add 3 mL of red cabbage juice. Stir. Note the color of the solution in your notebook. Be as descriptive as possible. Looking at an online color chart (Crayola Crayons?) may be helpful.
6. Repeat with the remaining solutions.
7. Dispose of these solutions in your waste beaker when done.

Part II Weak Acid Dilution and pH

1. **Stock Solution:** Obtain about 25-mL of the 0.500 M acetic acid solution in a clean, dry 50-mL beaker. Record the stock molarity in your notebook. Rinse the electrode by pouring a small portion of the acetic acid solution over the bulb portion of the pH electrode. Catch the rinse in a 600-mL beaker. **Measure and record the pH of this stock solution.** SAVE this solution for dilution in the NEXT STEP. Rinse the electrode thoroughly with deionized water and pat the outside of the electrode dry with a paper towel.
2. **Dilution 1:** Obtain a clean dry 100-mL graduated cylinder. Fill with the stock acetic acid solution to the 10.0 mL mark. Be as accurate as possible. Add deionized water to the 100.0 mL mark. Be as accurate as possible. This is the first 1:10 dilution. Pour this solution into a dry 250 mL beaker.

3. Rinse the electrode by pouring a small portion of this diluted acetic acid solution over the bulb portion of the pH electrode. Catch the rinse in a 600-mL beaker. **Measure and record the pH of this diluted solution.** SAVE this solution for dilution in the NEXT STEP. Rinse the electrode thoroughly with deionized water and pat the outside of the electrode dry with a paper towel.
4. **Dilution 2:** Obtain a second clean dry 100-ml graduated cylinder. Fill with the saved diluted acetic acid solution to the 10.0 mL mark. Be as accurate as possible. Add deionized water to the 100.0 mL mark. Be as accurate as possible. This is the second 1:10 dilution.
5. Rinse the electrode by pouring a small portion of this diluted acetic acid solution over the bulb portion of the pH electrode. Catch the rinse in a 600-mL beaker. **Measure and record the pH of this diluted solution.** Rinse the electrode thoroughly with deionized water and pat the outside of the electrode dry with a paper towel.
6. Discard all the acetic solutions into your waste beaker.
7. When you are finished, rinse the pH electrode and return it to the storage solution.
8. **Dispose of your waste beaker into the appropriate Hazardous Waste Bottle.**

TABLE 1: PH AND CLASSIFICATION OF SOLUTIONS

Complete this table based on your measured pH values in lab for each solution.

0.10 M Solution	Measured pH	Classify as acidic or basic	Classify as weak or strong	Calculate the solution $[H_3O^+]$	Calculate the solution $[OH^-]$	Calculate the solution pOH
HCl						
NaOH						
CH ₃ COOH						
NH ₃						
NH ₄ Cl						
Na ₂ CO ₃						
NaHCO ₃						
Na ₃ PO ₄						
Na ₂ HPO ₄						
NaH ₂ PO ₄						

For each weak acid or base write the K_a or K_b equilibrium CHEMICAL reaction. Calculate the % ionization or hydrolysis and the K_a or K_b of the acid or base using your results from the previous table as needed.

TABLE II – K_a AND K_b EQUATIONS AND VALUES FOR ACETIC ACID AND AMMONIA

WEAK Acidic or Basic Species	Write the K_a or K_b equilibrium chemical reaction	Calculated % ionization or % hydrolysis	Calculated K_a or K_b
CH ₃ COOH			
NH ₃			

TABLE III K_a AND % IONIZATION OF ACETIC ACID

Calculate $[H_3O^+]$, K_a , pK_a and the % ionization for the three solutions of acetic acid based on your pH measurement.

Solution	$[CH_3COOH]$ (M)	Measured pH	$[H_3O^+]$	% ionization	Calculated K_a	pK_a
Stock						
Dilution 1						
Dilution 2						

1. What is the trend in % ionization as the initial concentration of acetic acid decreases?

- 1.1. Do you think this trend would be the same for any weak acid? _____
2. What color(s) is red cabbage juice indicator in strong acids? In strong bases?
3. What color(s) is red cabbage juice indicator in weak acids? In weak bases?
4. Look again at table I. The last six solutions are salt solutions. Break each salt into ions and classify each ion as neutral, acidic or basic. NH_4Cl is done for you.

TABLE IV – ACIDIC AND BASIC IONS

WEAK Acidic or Basic Salts	Neutral Ion	Acidic Ion	Basic Ion
NH_4Cl	Cl^-	NH_4^+	None
Na_2CO_3			
NaHCO_3			
Na_3PO_4			
Na_2HPO_4			
NaH_2PO_4			

For each acid or basic ion, write the K_a or K_b equilibrium CHEMICAL reaction. Calculate the % ionization or hydrolysis and the K_a or K_b of the acidic or basic ion using your results from table I. See eqns 11-14. Identify the conjugate base/acid in each equilibrium and calculate the K_b (or K_a) value for the conjugate.

TABLE V – K_a AND K_b EQUATIONS AND VALUES FOR THE ACIDIC AND BASIC IONS AND THEIR CONJUGATES

WEAK Acidic or Basic Ion	K_a or K_b equilibrium chemical reaction	% Ionization or % hydrolysis	Calculated K_a or K_b	Conjugate Acid or Base	Conjugate K_a or K_b
NH_4^+	$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$			$\text{NH}_3(\text{aq})$	