Hydrolysis of Salts

#### **Background**

We expect solutions of substances such as HCl and HNO2 to be acidic and solutions of NaOH and NH3 to be basic. However, we may be somewhat surprised at first to discover that aqueous solutions of some salts such as NaNO2 and KC2H3O2 are basic, whereas others such as NH4Cl and FeCl3 are acidic. Recall that salts are the ionic products formed in neutralization reactions of acids and bases. For example, when NaOH and HNO2 (nitrous acid) react, the salt NaNO2 is formed:

NaOH *(aq)* + HNO2 *(aq)* → NaNO2 *(aq)* + H2O *(l)*

Nearly all salts are strong electrolytes and exist as ions in aqueous solutions. Many ions react with water to produce acidic or basic solutions. The reactions of ions with water are frequently called *hydrolysis reactions*. We will see that anions such as CN‾ and C2H3O2‾ that are the conjugate bases of the weak acids HCN and HC2H3O2, respectively, react with water to form OH‾ ions. Cations such as NH4+ and Fe3+ come from weak bases and react with water to form H+ ions.

**Hydrolysis of Anions: Basic Salts**

Anions of weak acids react with proton sources. When placed in water these anions react to some extent with water to accept protons and generate OH– ions and thus cause the solution pH to be greater than 7. Recall that proton acceptors are BrØnsted-Lowry bases. Thus, the anions of weak acids are basic in two senses: they are proton acceptors, and their aqueous solutions have pH’s above 7. The nitrite ion, for example, reacts with water to increase the concentration of OH– ions:

NO2‾ *(aq)* + H2O *(l)* ⇌ HNO2 *(aq)* + OH‾ *(aq)*

This reaction of nitrite ion is similar to that of weak bases such as NH3 with water:

NH3 *(aq)* + H2O *(l)* ⇌ NH4+ *(aq)* + OH‾ *(aq)*

Thus, both NH3 and NO2‾ are bases and as such have a basicity or base-dissociation constant, *Kb*, associated with their corresponding equilibria. According to the BrØnsted-Lowry theory, the nitrite ion is the conjugate base of nitrous acid. Let’s consider the conjugate acid-base pair HNO2 and NO2‾ and their behavior in water:

HNO2 ⇌ H+ + NO2‾ *Ka* = [H+] [NO2‾]

[HNO2]

NO2**–** *(aq)* + H2O *(l)* ⇌ HNO2 *(aq)* + OH‾ *(aq)* *Kb* = [HNO2] [OH‾]

[NO2‾]

Multiplication of these ionization constants yields: *Ka* × *Kb*  = [H+] [OH‾] = *Kw*  = 1.0 × 10‾14

(*where Kw is the ion-product constant of water*)

***Thus, the product of the acid-ionization constant for an acid and the base-dissociation constant for its conjugate base is the ion-product constant for water: Ka × Kb  = Kw  = 1.0 × 10‾14***

Knowing the K*a* for a weak acid, the K*b* for the anion of the acid (conjugate base) can be found: K*b* = K*w*/K*a*

A table of acid-ionization constants can be found in Appendix II of your text. The K*a* for nitrous acid, HNO2, is 4.5 x 10−4, thus we can calculate K*b* for NO2−. K*b* = (1.0 x 10−14)/(4.5 x 10−4) = 2.2 x 10−11

*We note that the stronger the acid is, the larger its Ka, and the weaker its conjugate base, the smaller its Kb. Likewise, the weaker the acid (the smaller the Ka), the stronger the conjugate base (the larger the Kb).*

***Anions*** derived from ***strong acids***, such as Cl‾ from HCl, do **NOT** react with water to affect the pH. Other examples: Br‾, I‾, NO3‾, SO42‾, and ClO4‾ They are spectator ions in the acid-base sense and can be described as *neutral* ions. Similarly, ***cations*** from ***strong bases***, such as Na+ from NaOH or K+ from KOH, do not react with water to affect the pH. *Hydrolysis of an anion occurs only when it can form a molecule or ion that is a weak electrolyte in reaction with water.* Strong acids and bases do not exist as molecules in dilute water solutions.

*Example 1:* What is the pH of a 0.10M NaClO solution if *Ka* for HClO is 3.0 x 10−8 ?

The salt NaClO exists as Na+ and ClO−. The Na+ ions are spectator ions, but ClO− ions undergo hydrolysis to form the weak acid HClO. Let x equal the equilibrium concentration of HClO (and OH−):

ClO‾ *(aq)* + H2O *(l)* ⇌ HClO *(aq)* + OH‾ *(aq)* The value of K*b* for this reaction can be calculated

0.10M 0 0 K*b* = (1.0 x 10−14/3.0 x 10−8) = 3.3 x 10−7

-x +x +x Because K*b* is so small compared to 0.10, we can

0.10 –x x x neglect x, thus 0.10 – x ≈ 0.10

*Kb* = [HNO2] [OH‾] x2 = 3.3 x 10−7 x = 1.8 x 10−4 M pOH = -log[OH−] pOH = 3.74

[NO2‾] 0.10 pH = 10.26

Anions with ionizable protons such as HCO3−, H2PO4−, and HPO42− may be either acidic or basic, depending on the relative values of K*a* and K*b* for the ion. We will NOT consider such ions in this experiment.

**Hydrolysis of Cations: Acidic Salts**

Cations that are derived from weak bases react with water to increase the hydrogen-ion concentration; they form acidic solutions. The ammonium ion is derived from the weak base NH3 and reacts with water as follows: NH4+ *(aq)* + H2O *(l)* ⇌ H3O+ *(aq)* + NH3 *(aq)*

This reaction is completely analogous to the dissociation of any other weak acid, such as HC2H3O2 or HNO2. We can represent this acid-ionization of NH4+ more simply as: NH4+  ⇌ NH3 *(aq)* + H+ *(aq)*

The acid-ionization constant of NH4+ is related to the *Kb* of NH3, which is the conjugate base of NH4+:

NH3 *(aq)* + H2O *(l)* ⇌ NH4+ *(aq)* + OH‾ *(aq) Kb* = 1.76 x 10−5

Thus K*a* (NH4+) = (1.0 x 10−14/1.76 x 10−5) = 5.68 x 10−10

Cations of the alkali metals (Group 1A) and the larger alkaline earth ions, Ca2+, Sr2+, and Ba2+, do not react with water, because they come from strong bases. Thus these ions have no influence on the pH of aqueous solutions. They are merely spectator ions. Consequently, they are described as being neutral in the acid-base sense. The cations of most other metals do hydrolyze to produce acidic solutions. Metal cations are coordinated with water molecules, and it is the hydrated ion that serves as the proton donor. The following equation illustrate this behavior for the hexaaqua iron (III) ion:

Fe(H2O)63+ *(aq)* + H2O *(l)* ⇌ Fe(H2O)5(OH)2+ *(aq)* + H3O+ *(aq)*

We frequently omit the coordinated water molecules from such equations. For example:

Fe3+ *(aq)* + H2O *(l)* ⇌ Fe(OH)2+ *(aq)* + H+ *(aq)*

Additional hydrolysis reactions can occur to form Fe(OH)2+ and even lead to the precipitation of Fe(OH)3. The equilibria for such cations are often complex, and not all species have been identified. However, these equations serve to illustrate the acidic character of dipositive and tripositive ions and account for most of the H+ in these solutions. ­­

##### *Summary of Hydrolysis Behavior of Salts*

Whether a solution of a salt will be acidic, neutral or basic can be predicted on the basis of the strengths of the acid and base from which the salts was formed.

1. *Salt of a strong acid and a strong base:* Examples: NaCl, KBr, and Ba(NO3)2. Neither the cation nor anion hydrolyzes, and the solution has a pH of 7.
2. *Salt of a strong acid and a weak base:* Examples: NH4Br, ZnCl2, and Al(NO3)3. The ***cation*** hydrolyzes, forming H+ ions, and the solution has a pH less than 7 *(acidic)*.
3. *Salt of a weak acid and a strong base:* Examples: NaNO2, KC2H3O2, and Ca(OCl)2. The ***anion*** hydrolyzes, forming OH‾ ions, and the solution has a pH greater than 7 *(basic)*.
4. *Salt of a weak acid and a weak base:* Examples: NH4F, NH4C2H3O2, and Zn(NO2)2. Both ions hydrolyze. The pH of solution is determined by the relative extent to which each ion hydrolyzes.

In this experiment, we will test the pH of water and of several aqueous salt solutions to determine whether these solutions are acidic, basic, or neutral. In each case, the salt solution will be 0.1 *M*. Knowing the concentration of the salt solution and the measured pH of each solution allows us to calculate *Ka* or *Kb* for the ion that hydrolyzes.

*Example 2:* Calculate K*b* for OBr− if a 0.10M solution of NaOBr has a pH of 10.85.

The spectator ion is Na+. Alkali metal ions do not react with water and have no influence on pH. The ion OBr− is an anion of a weak acid and thus reacts with water to produce OH− ions: OBr− + H2O ⇋ HOBr + OH−

and the corresponding expression for the base dissociation constant is *Kb* = [HOBr] [OH‾]

If the pH is 10.85, then pOH =14-10.85 = 3.15 and [OBr‾]

[OH−] = 10(-3.15) = 7.1 x 10−4M The concentration of HOBr that is formed is also 7.1 x 10−4M. The [OBr−] =0.10M - 7.1 x 10−4M ≈ 0.10M Substituting the values into the *Kb* expression gives *Kb* = 5.0 x 10−6

We will use a set of indicators to determine the pH of various salt solutions. The dark areas in the figure denote the transition ranges for the indicators. We will generally find that solutions we test will be more acidic that we would predict them to be. A major reason for this increased acidity is the occurrence of CO2 dissolved in the solutions. CO2 reacts with the water to generate H+:

CO2 *(g)* + H2O *(l)* ⇌ H2CO3 *(aq)* ⇋ H+*(aq)* + HCO3−*(aq)* The solubility of CO2 is greatest in basic solutions, intermediate in neutral solutions and least in acidic solutions. Even distilled water will therefore be somewhat acidic unless it is boiled to remove the dissolved CO2.

**HYDROLYSIS OF SALTS DIRECTIONS**

Obtain 2 CLEAN well plates. (Plates have been washed and then rinsed with boiled distilled water.) Place them on a piece of white paper as shown by your instructor. Using your data table as a guide, fill each well across the ***ROW*** about half full (be consistent) with the solution to be tested. *Note: all salt solutions are 0.10M* Continue until all of the rows are completed. Add one drop of the indicator to the wells in each ***COLUMN*** as shown on the data table. Continue until each indicator has been added to the appropriate wells in the COLUMNS. You may use a toothpick to stir the solutions in the wells if necessary. Just remember rinse the toothpick with distilled water and dry it before stirring the next solution. Complete the data table by recording the color of each well. Empty the well plates into your sink and wash them thoroughly. Rinse them with distilled water, shake them out and allow them to dry.

Interpret your results by using the indicator color charts to estimate the pH (to the nearest 0.1) of each solution. Each lab group *MAY* be assigned to verify the pH of 1-2 salt solutions using the pH probes and Labquests. This data will be shared during class discussion. Using your estimated pH values, calculate the H+ and OH- ion concentrations for each solution and record the value in the data table. Complete the analysis.



