IV) Hydrolysis

March 5, 2018 1:48 PM

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When any acid (strong or weak) reacts with a strong hydroxide base, the reaction is 100% (due to the strong base): → drives FWD rxn.

Examples:

$2\,HBr_{(aq)} + Ca(OH)_{2(aq)} \Rightarrow 2H_2O_{(l)} + CaBr_{2(aq)}$ (s. acid; salt)

$CH_3COOH + KOH \Rightarrow H_2O_{(l)} + KCH_3COO_{(aq)}$ (weak acid.)

In general, the products are water and salt.
These reactions are called neutralization reactions.

When a strong acid reacts with a base that does not contain hydroxide, it is still a neutralization reaction, however the only product is a salt. The reaction is 100% because a strong acid is reacting. (→ weak base) (no OH^- = not H_2O)

Example:

$HCl_{(aq)} + NH_{3(aq)} \Rightarrow NH_4Cl_{(aq)}$ (H^+)

↑ NH_4^+ always soluble

The salts that are produced can be soluble or insoluble (use your solubility table). The insoluble salts will form a solid and precipitate out of solution. The soluble salts will stay in solution as cations and anions and may act as weak acids or bases. For example, the salt produced above was $NH_4Cl_{(aq)}$. (salt + dissoc. 100%.)
Is it soluble (use your solubility table)?

→ yes, NH_4^+ always (aq)

Therefore, how will it actually exist in solution?

$NH_4Cl_{(aq)} \xrightarrow{\text{dissoc. } 100\%} NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$

Is the cation or anion a weak acid or base?

weak acid. (NH_4^+)

conj. base of strong acid (not really a base) (Cl^-)

So what will that ion do in solution?

(aq) = dissolved in H_2O

weak (∴ equilibrium)

$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + NH_3{}_{(aq)}$

weak acid. ~5%.

The reaction you just wrote above is a **hydrolysis reaction**, and it can cause salt solutions to be acidic or basic (acidic in the example above due to H_3O^+ formation).

So, whenever a salt is dissolved in solution OR whenever a salt is formed due to an acid reacting with a base, the resulting salt solution may be acidic or basic if a **hydrolysis** reaction occurs. If not, the solution will be neutral.

= (not always ... some ⊕ and ⊖ ions are not weak acids or weak bases)

The ions that make up the salts produced from the neutralization reactions may or may not undergo hydrolysis. Here are the guidelines:

1. Ions that will not undergo hydrolysis are... (⊖ spectator ions)

- conjugate bases of strong acids (b/c not really bases) → one-way rxn.

Cl^-, Br^-, I^-, NO_3^-, ClO_4^-

(exception: HSO_4^- is NOT a base ... but it IS a weak acid, so it will hydrolyze acidically)

2. Ions that will not undergo hydrolysis are... (⊕ spectator ions)

- conjugate acids of strong bases (b/c they are not really acids)

Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} (group 1 + 2 cations)

(exception: OH^- (strong base) and NH_3 (weak base) are not acids at all.)

hydrolysis !! :)

3. Ions that will undergo hydrolysis are… weak acids + weak bases that exist at equilibrium.

Write a dissociation equation for each salt, and then predict whether the resulting salt solutions will be acidic, basic, or neutral, and write any hydrolysis equations as support.

neutralization rxn → product (salt)

1. $KCl_{(aq)} \longrightarrow K^+_{(aq)} + Cl^-_{(aq)}$

both soluble spectator ion ∴ NO hydrolysis.

2. $NH_4NO_{3(aq)} \longrightarrow NH_4^+_{(aq)} + NO_3^-_{(aq)}$

spect. ion (conj. base of strong acid)

hydrolysis of a salt: rxn between water and the cation/anion

weak acid. hydrolysis rxn: $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$

acid weak base.

= ACIDIC solution

3. $Na_2CO_{3(aq)} \longrightarrow Na^+_{(aq)} + CO_3^{2-}_{(aq)}$

spect. ion; weak base

will hydrolyze: $CO_3^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^- + OH^-$

weak acid; strong base

BASIC solution

Sometimes, an ion is ***amphiprotic***, so will it act more as an acid or a base?

(salt)

4. $NaHSO_{3(aq)} \longrightarrow Na^+_{(aq)} + HSO_3^-_{(aq)}$

spec.

amphiprotic ∴ must hydrolyze BOTH WAYS!

acidic hydrolysis: (HSO_3^- will act as an acid) $HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^-$

Ka

acting as acid: $K_a = 1.0\times10^{-7}$ ✓

basic hydrolysis: (HSO_3^- will act as a base) $HSO_3^- + H_2O \rightleftharpoons OH^- + H_2SO_3$

Kb; Ka of conj. acid.

acting as base: $K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{1.5\times10^{-2}}$

$K_b = 6.7\times10^{-13}$ X

compare Ka to Kb: Ka > Kb ∴ HSO_3^- will hydrolyze acidically

5. $KHCO_{3(aq)} \longrightarrow K^+_{(aq)} + HCO_3^-_{(aq)}$

spectator.

acid hydrolysis: $HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$

Ka

$K_a = 5.6\times10^{-11}$ X occur very little

basic hydrolysis: $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$

Kb; Ka of conj. acid.

$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{4.3\times10^{-7}}$ more!

basic hydrolysis: $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$ $K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{4.3\times10^{-7}}$ more!

K_a of conj. acid. $K_b = 2.3\times10^{-8}$

* $K_b > K_a$ ∴ Basic Hydrolysis

If an ion is amphiprotic, write an acidic hydrolysis with a K_a value, and a basic hydrolysis with a K_b value. Whichever K value is greater, that reaction will occur to a greater extent.

How do you predict if the solution is acidic or basic when both ions in the salt hydrolyze? (similar to the amphiprotic)

salt

6. $NH_4NO_{2(aq)} \longrightarrow NH_4^+{}_{(aq)} + NO_2^-{}_{(aq)}$

acid hydrolysis / basic hydrolysis

no spectator ions.
NH_4^+ – weak acid
NO_2^- – weak base

$NH_4^+ + H_2O \rightleftharpoons H_3O^+_{(aq)} + NH_{3(aq)}$ $K_a = 5.6\times10^{-10}$

$NO_2^- + H_2O \rightleftharpoons HNO_{2(aq)} + OH^-$ $K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{4.6\times10^{-4}} = 2.2\times10^{-11}$

conj. acid.

since $K_a > K_b$, the acid hydrolysis will occur to a greater extent.

7. $Al(NO_2)_{3(aq)} \rightarrow Al^{3+} + NO_2^-$

*when Al^{3+}, Cr^{3+}, or Fe^{3+} exist in solution, they will gain six water molecules around them and then act as a weak acid (see table).

$Al(H_2O)_6^{3+}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Al(H_2O)_5(OH)^{2+}_{(aq)}$ (H^+ transferred)

$K_a = 1.4\times10^{-5}$

$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$ $K_b = 2.2\times10^{-11}$ (calc 4)

$K_a > K_b$ ∴ acidic hydrolysis.

Summarize how you can predict whether a salt solution with two ions that hydrolyze will be acidic, basic, or neutral:

$K_a > K_b$ = acidic

$K_b > K_a$ = basic

$K_a = K_b$ = neutral.

Assignment 5: Hydrolysis Exercises

1. Hydrolysis Mini-Lab – answer the questions from the lab for #1 of this assignment.

2. Write dissociation equations, and any hydrolysis equation(s) occurring when the following salts are added to water and predict whether the resulting solution will be acidic, basic, or neutral.

   a. Na_2HPO_4 b. $Cr(SO_4)_3$

3. NH_3 is titrated with HI. When the two react in the titration, what salt is formed? Does the salt undergo hydrolysis? If so, what is the hydrolysis equation and will the resulting pH be above or below 7?

4. In a titration, which of the following combinations would result in an equivalence point with pH greater than 7.0? *Hint: find the resulting salt from each reaction and see if and how it undergoes hydrolysis
   A. HCl and NaOH
   B. HNO_3 and NH_3
   C. HBr and $NaCH_3COO$
   D. CH_3COOH and NaOH

5. Calculate the pH of a 0.20M KCN solution (Type 1 K_b problem after considering hydrolysis).