Acid-Base Character of Salt Solutions

The pH of a salt solution will depend on the acidbase nature of both the cation and anion.

Cations

Cations are potentially acidic, but some have no effect on pH.

$$M(H_2O)_6^{n+} + H_2O \Rightarrow H_3O^+ + M(H_2O)_5OH^{(n-1)+}$$

- Metal cations with high charge density are acidic in water; e.g., $Al(H_2O)_6^{3+}$, $Fe(H_2O)_6^{3+}$.
- ✓ Metal cations with low charge density are neutral in water; e.g., Na⁺, K⁺, Rb⁺, Cs⁺, Sr²⁺, Ba²⁺.
- ✓ Polyatomic cations that are conjugate acids of molecular weak bases are acidic; e.g., NH₄⁺, CH₃NH₂⁺.

Acid-Base Character of Salt Solutions Anions

Anions that are not acid anions are potentially basic, but some have no effect on pH.

$$X^- + H_2O \rightleftharpoons HX + OH^-$$

- ✓ Aprotic conjugate bases of weak acids are basic in water; e.g., OAc⁻, OCl⁻, F⁻, NO₂⁻, CN⁻, SO₄²⁻, SO₃²⁻, CO₃²⁻.
- ✓ Aprotic conjugate bases of strong acids are neutral in water; e.g., Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻.

Acid-Base Character of Acid Anions

- Acid anions (which are generally amphiprotic) may be acidic or basic, depending on the relative magnitudes of their K_a and K_b values.
 - ✓ If $K_a > K_b$, the acid anion will be acidic; e.g., HSO_4^- , HSO_3^- , $H_2PO_4^-$
 - If $K_b > K_a$, the acid anion will be basic; e.g., HCO_3^- , HS^- , HPO_4^-

Reactions Between Two Conjugate Acid-Base Pairs

What happens when two solutions, each containing different conjugate acid-base pairs, are mixed together?

✓ The two acids will compete to donate protons, and the two bases will compete to accept protons.

An equilibrium will be established between the stronger acid and the stronger base in the direction favoring formation of the weaker conjugate base and weaker conjugate acid.

$$HC1 + H_2O \rightleftharpoons C1^- + H_3O^+$$

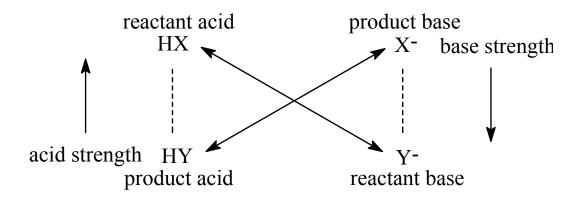
Acid strengths: $HCl > H_3O^+$ Base strengths: $H_2O > Cl^ \Rightarrow$ Equilibrium lies right.

$$HOAc + H_2O \Rightarrow OAc^- + H_3O^+$$

Acid strengths: $H_3O^+ > HOAc$ Base strengths: $OAc^- > H_2O$ \Rightarrow Equilibrium lies left.

Predicting Reactions with an Ordered Acid-Base Table

The favored equilibrium will be between the acid that lies higher in the left column and the base that lies lower in the right column, to produce the conjugates in the upper right and lower left.



pH After Neutralization

- The reaction of an acid with a stoichiometrically equivalent amount of a base is called *neutralization*.
- ✓ The pH of the solution following a neutralization depends upon the acid and base strengths of the products of the reaction, which in turn depend upon the acid and base strengths of the original reactants.

Strong Acid + Strong Base

- The reaction is between the hydronium ion produced by the acid and the hydroxide ion produced by the base.
- For any strong acid-strong base neutralization, the net ionic equation is

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

Neutralization produces a neutral solution (pH = 7).

Example: $HNO_3(aq) + NaOH(aq)$

Molecular equation:

$$HNO_3(aq) + NaOH(aq) \rightarrow H_2O(l) + NaNO_3(aq)$$

Ionic equation:

$$H_3O^+(aq) + NO_3^-(aq) + Na^+(aq) + OH^-(aq)$$

 $\rightarrow 2 H_2O(l) + Na^+(aq) + NO_3^-(aq)$

Net ionic equation:

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2 H_2O(l)$$

Weak Acid + Strong Base

- All of the weak acid is converted into an equivalent amount of its conjugate base, which is basic.
- Neutralization produces a basic solution (pH > 7).

Example:

Molecular equation:

$$HOAc(aq) + NaOH(aq) \rightarrow H_2O(l) + NaOAc(aq)$$

Ionic equation:

$$HOAc(aq) + Na^{+}(aq) + OH^{-}(aq)$$

 $\rightarrow H_2O(l) + Na^{+}(aq) + OAc^{-}(aq)$

Net ionic equation:

$$HOAc(aq) + OH^{-}(aq) \rightarrow H_2O(l) + OAc^{-}(aq)$$

The back reaction to the neutralization produces the basic pH:

$$OAc^- + H_2O \Rightarrow HOAc + OH^-$$

$$K_b(\text{OAc}^-) = K_w / K_a(\text{HOAc}) = 5.65 \text{ x } 10^{-10}$$

Weak Base + Strong Acid

- All of the weak base is converted into an equivalent amount of its conjugate acid, which is acidic.
- Neutralization produces an acidic solution (pH < 7).

Example:

Molecular equation:

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$

Ionic equation:

$$NH_3(aq) + H_3O^+(aq) + Cl^-(aq)$$

 $\rightarrow NH_4^+(aq) + H_2O(l) + Cl^-(aq)$

Net ionic equation:

$$NH_3(aq) + H_3O^+(aq) \rightarrow NH_4^+(aq) + H_2O(l)$$

The back reaction to the neutralization produces the acidic pH:

$$NH_4^+ + H_2O \Rightarrow NH_3 + H_3O^+$$

$$K_a(NH_4^+) = K_w/K_b(NH_3) = 5.65 \times 10^{-10}$$

Neutralization Between a Weak Acid and Weak Base

- The pH of the resulting solution will depend upon the relative magnitudes of the K_b and K_a of the conjugates produced in the neutralization.
- The resulting species with the larger K value will determine whether the solution is acidic or basic.

$$HF(aq) + NH_3(aq) \Rightarrow F^-(aq) + NH_4^+(aq)$$

 $K_a = K_b = K_b = K_a =$
 6.8×10^{-4} 1.8×10^{-5} 1.5×10^{-11} 5.6×10^{-10}

$$K_a(NH_4^+) > K_b(F^-) \to pH < 7$$