# Using $K_a$ to Calculate pH

- Percent ionization relates the equilibrium $H^+$ concentration, $[H^+]_{eqm}$, to the initial HA concentration, $[HA]_0$.
- The higher percent ionization, the stronger the acid.
- Percent ionization of a weak acid decreases as the molarity of the solution increases.
- For acetic acid, 0.05 *M* solution is 2.0 % ionized whereas a 0.15 *M* solution is 1.0 % ionized.
- Use ICE Charts to determine $[H^+]$
- $-\log [H^+] = pH$

Substitute into the equilibrium constant expression and solve.

Remember to turn *x* into pH if necessary.

**Examples –** Calculate pH, pOH and percent dissociation for each of the following:

1. 0.35 M HF ($K_a = 7.2 \times 10^{-4}$)

   pH = 1.80, pOH = 12.20, 4.5% ionized

2. 0.62 M $NH_4^+$ (from $NH_4Cl$) ($K_a = 5.6 \times 10^{-10}$)

   pH = 4.73, pOH = 9.27, .0030% ionized

# Polyprotic Acids

- Polyprotic acids have more than one ionizable proton.
- The protons are removed in steps not all at once:

$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \qquad K_{a1} = 1.7 \times 10^{-2}$$

$$HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \qquad K_{a2} = 6.4 \times 10^{-8}$$

- It is always easier to remove the first proton in a polyprotic acid than the second.
- Therefore, $K_{a1} > K_{a2} > K_{a3}$ etc.
- For calculations, we will generally only consider the first dissociation (the others contribute very little to $[H^+]$
  - EXCEPTION: $H_2SO_4$

# Dilute Sulfuric Acid Solutions

- First Dissociation is Strong (large $K_a$)
- Second Dissociation is weak ($K_{a2} = 1.2 \times 10^{-2}$)
  - Make ICE chart for second dissociation – initial $[H^+]$ is equal to initial $[HSO_4^-]$
  - Determine x (using quadratic if necessary)
  - Solve for $[H^+]_{eq}$

# Polyprotic Acids

**TABLE 16.3 Acid-Dissociation Constants of Some Common Polyprotic Acids**

| Name | Formula | $K_{a1}$ | $K_{a2}$ | $K_{a3}$ |
|---|---|---|---|---|
| Ascorbic | $H_2C_6H_6O_6$ | $8.0 * 10^{-5}$ | $1.6 * 10^{-12}$ | |
| Carbonic | $H_2CO_3$ | $4.3 * 10^{-7}$ | $5.6 * 10^{-11}$ | |
| Citric | $H_3C_6H_5O_7$ | $7.4 * 10^{-4}$ | $1.7 * 10^{-5}$ | $4.0 * 10^{-7}$ |
| Oxalic | $H_2C_2O_4$ | $5.9 * 10^{-2}$ | $6.4 * 10^{-5}$ | |
| Phosphoric | $H_3PO_4$ | $7.5 * 10^{-3}$ | $6.2 * 10^{-8}$ | $4.2 * 10^{-13}$ |
| Sulfurous | $H_2SO_3$ | $1.7 * 10^{-2}$ | $6.4 * 10^{-8}$ | |
| Sulfuric | $H_2SO_4$ | Large | $1.2 * 10^{-2}$ | |
| Tartaric | $H_2C_4H_4O_6$ | $1.0 * 10^{-3}$ | $4.6 * 10^{-5}$ | |

**Examples:** Calculate pH, pOH, and % dissociation

1. 0.15 M $H_3PO_4$

   pH = 1.47, pOH = 12.53, 22% ionized

2. 0.30 M $NaH_2PO_4$

   pH = 3.87, pOH = 10.13, .045% ionized

3. 0.61 M $H_2CO_3$

   pH = 3.29, pOH = 10.71, .084% ionized

# Weak Bases

- Weak bases remove protons from substances.
- There is an equilibrium between the base and the resulting ions:

$$\text{Weak base} + H_2O \rightleftharpoons \text{conjugate acid} + OH^-$$

- Example:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

- The base dissociation constant, $K_b$, is defined as

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

# Types of Weak Bases

- Bases generally have lone pairs or negative charges in order to attack protons.
- Most neutral weak bases contain nitrogen.
- Amines are related to ammonia and have one or more N-H bonds replaced with N-C bonds (e.g., $CH_3NH_2$ is methylamine).
- Anions of weak acids are also weak bases. Example: $OCl^-$ is the conjugate base of HOCl (weak acid):

$$ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq) \quad K_b = 3.3 \times 10^{-7}$$

## Calculating pH and pOH of Weak Base Solutions

- Use ICE Chart to determine $[OH^-]_{eq}$
- Use $[OH^-]$ to find pOH, and thus pH

**Examples – Calculate pOH and pH of each of the following solutions:**

1. 0.15 M $NH_3$ ($K_b = 1.8 \times 10^{-5}$)

   pH = 11.22 pOH = 2.78

2. 0.38 M $HONH_2$ ($K_b = 1.1 \times 10^{-8}$)

   pH = 9.81 pOH = 4.19

# Relationship Between $K_a$ and $K_b$

- We need to quantify the relationship between strength of acid and conjugate base.
- When two reactions are added to give a third, the equilibrium constant for the third reaction is the product of the equilibrium constants for the first two:

Reaction 1 + reaction 2 = reaction 3

has

$$K_3 = K_1 \times K_2$$

- For a conjugate acid-base pair

$$K_w = K_a \times K_b$$

- Therefore, the larger the $K_a$, the smaller the $K_b$. That is, the stronger the acid, the weaker the conjugate base.
- Taking negative logarithms:

$$pK_w = pK_a + pK_b$$

## TABLE 16.5 Some Conjugate Acid-Base Pairs

| Acid | $K_a$ | Base | $K_b$ |
|---|---|---|---|
| $HNO_3$ | (Strong acid) | $NO_3^-$ | (Negligible basicity) |
| $HF$ | $6.8 * 10^{-4}$ | $F^-$ | $1.5 * 10^{-11}$ |
| $HC_2H_3O_2$ | $1.8 * 10^{-5}$ | $C_2H_3O_2^-$ | $5.6 * 10^{-10}$ |
| $H_2CO_3$ | $4.3 * 10^{-7}$ | $HCO_3^-$ | $2.3 * 10^{-8}$ |
| $NH_4^+$ | $5.6 * 10^{-10}$ | $NH_3$ | $1.8 * 10^{-5}$ |
| $HCO_3^-$ | $5.6 * 10^{-11}$ | $CO_3^{2-}$ | $1.8 * 10^{-4}$ |
| $OH^-$ | (Negligible acidity) | $O^{2-}$ | (Strong base) |

# Acid-Base Properties of Salt Solutions

- Nearly all salts are strong electrolytes.
- Therefore, salts exist entirely of ions in solution.
- Acid-base properties of salts are a consequence of the reaction of their *ions* in solution.
- The reaction in which ions produce $H^+$ or $OH^-$ in water is called hydrolysis.
- Anions from weak acids are basic.
- Anions from strong acids are neutral.

# An Anion's Ability to React with Water

- Anions, $X^-$, can be considered conjugate bases from acids, HX.
- If $X^-$ comes from a strong acid, then it is neutral.
- If $X^-$ comes from a weak acid, then

$$X^-(aq) + H_2O(l) \rightleftharpoons HX(aq) + OH^-(aq)$$

- The pH of the solution can be calculated using equilibrium!

## A Cation's Ability to React with Water

- Polyatomic cations with ionizable protons can be considered conjugate acids of weak bases.

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

- Some metal ions react in solution to lower pH.

## Combined Effect of Cation and Anion in Solution

- An anion from a strong acid has no acid-base properties.
- An anion that is the conjugate base of a weak acid will cause an increase in pH (basic ion).

- A cation that is the conjugate acid of a weak base will cause a decrease in the pH of the solution (acidic ion).
- Metal ions will cause a decrease in pH **except for the alkali metals and alkaline earth metals**.
- When a solution contains both cations and anions from weak acids and bases, use $K_a$ and $K_b$ to determine the final pH of the solution.
- Use ICE charts to calculate pH and pOH (as for weak acid and weak base solutions)

# Amphoteric Substances

- Determine $K_a$ and $K_b$ for the substance (ion)
- If $K_a > K_b$, then the ion is acidic
- If $K_a < K_b$, then the ion is basic
- Use the appropriate constant to calculate pH and pOH

**Examples – State whether each will be acidic, basic, or neutral in aqueous solution:**

1. NaOCl
2. $Fe(NO_3)_3$
3. KBr
4. $LiClO_4$
5. $NaHCO_3$
6. $CaCl_2$
7. $NH_4NO_3$
8. $NiI_2$

**Examples – State whether each will be acidic, basic, or neutral in aqueous solution:**

1. $NaOCl$ basic
2. $Fe(NO_3)_3$ acidic
3. $KBr$ neutral
4. $LiClO_4$ neutral
5. $NaHCO_3$ basic
6. $CaCl_2$ neutral
7. $NH_4NO_3$ acidic
8. $NiI_2$ acidic

**Examples – Calculate pH and pOH for each solution:**

1. 0.25 M $NH_4Cl$

2. 0.60 M KBr

3. 0.18 M $KC_2H_3O_2$

4. 0.50 M $NaHCO_3$

1.