
Acids, Bases, and Salts

General Chemistry

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I. Definitions

The terms acid, base and salt are attempts to classify and organize reactions - these terms are used to model the behavior of species in solution

A. Arrhenius [®] an attempt to understand the behavior of electrolytes in water

Acids give H^+ in water	$H^+ A^-$
Bases give OH^- in water	$M^+(OH)^-$
Salts are combinations of acids and bases	$M^+ A^-$

B. Bronsted-Lowry [®] An attempt to be more general and operational so the model could be applied to other solvent systems

Acids are proton donors

Bases are proton acceptors

Salts are combinations of acids and bases.

- **The Bronsted-Lowry model allows us to analyze a reaction operationally - that is, how each molecule is acting toward the other.**
- **(Examples)**

II. Terms and Types

A. <i>Acids</i>	HA	anions with H^+
<i>Bases</i>	$M^+(OH)^-$	metal ions with hydroxides
	NH_3 and derivatives	
B. <i>Monoprotic acid</i>		one H^+ (HCl)
<i>Polyprotic acid</i>		more than one H^+ (H_2CO_3)
<i>Monobasic</i>		one OH^- (NaOH)
<i>Dibasic</i>		more than one OH^- [$Ca(OH)_2$]
<i>Amphiprotic</i>		can accept or lose H^+ (H_2O, HCO_3^-, $H_2PO_4^-$)

C. Naming

Binary acid (2 element acid, H and a nonmetal)

Acid name

Anion name

hydro_____ic acid

_____ide

Ternary acid (3 element acid; H,O and nonmetal)

Acid name

Anion name

per_____ic acid

per_____ate

_____ic acid

_____ate

_____ous acid

_____ite

hypo_____ous acid

hypo_____ite

III. Strengths in Water

A. Acids

- **Strong (ionize 100%)**
- **Weak (ionize < 100%)**

B. Bases

- **Strong (ionize 100%)**
- **Weak (ionize <100%)**

Also, the stronger the acid, the weaker is its CB

Also, the stronger the base, the weaker is its CA

C. Rules for predicting strength

- 1. Binary acids** HBr, HCl, HI are strong, the rest are weak
- 2. Ternary acids** HClO₃, HClO₄, HNO₃, and the first ionization of H₂SO₄ are strong, the other inorganic acids are weak, all organic acids are weak
- 3. Polyprotic acids** -the 2nd and subsequent ionizations are weak. Thus any anion with ionizable hydrogens derived from a polyprotic acid is a weak acid.
- 4. Metallic bases** Group IA and IIA hydroxides (except Be) are strong but the solubility of calcium hydroxide and magnesium hydroxide are limited
- 5. NH₃ and all organic amines are weak bases.**

D. Writing reactions of acids, bases and salts in water



Hydrolysis reactions may also occur with M^+ and A^- in water. We will cover these later.

IV. pH and K_w

A. pH is a measure of acidity, pOH is a measure of basicity

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] \qquad [\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

$$\text{pOH} = -\log_{10}[\text{OH}^-] \qquad [\text{OH}^-] = 10^{-\text{pOH}}$$

B. Dissociation of water



$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 1.00 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

acid $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ pH < 7

neutral $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ pH = 7

basic $[\text{H}_3\text{O}^+] < [\text{OH}^-]$ pH > 7

V. Acid/Base Equilibria

A. Weak Acids



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Polyprotic acids have several K_a 's - as many as there are ionizable H's.

B. Weak Bases



$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

C. Types of problems

1. Find K_a from pH (or K_b from pOH)

- *Find the acid dissociation constant for a weak monoprotic acid of concentration 0.10 M if the pH of the solution is 2.94.*

2. Find the pH (or pOH) from K_a (or K_b)

- *Find the pH of a 0.10 M weak monoprotic acid solution. The acid has a K_a of 1.8×10^{-5} .*

Note - this type of problem involves the possible solution of a quadratic equation (2nd order polynomial). A good rule of thumb is -

If $[\text{original acid}]/K_a = 100$ or more then neglect $-x$ in the denominator of the equilibrium expression.

A related quantity often solved for in these types of problems is the % ionization

$$\% \text{ ionization} = (\text{amt ionized} / [\text{orig}]) \cdot 100$$

3. Polyprotic acids

- **What is the pH and the oxalate ion concentration of a 0.10M solution of oxalic acid? $K_{a1} = 5.9 \times 10^{-2}$, $K_{a2} = 6.4 \times 10^{-5}$.**

There are two equilibria but notice that there is a factor of almost 1000 between the first and second ionization. Because of this large difference the amount of H_3O^+ and $HC_2O_4^-$ will be determined by the first ionization alone. Most polyprotic acids will have this behavior.

The first ionization still gives us problems because the ionization constant is so large. This means that we must solve the equation using the quadratic formula or the method of successive approximations. The second ionization expression can be easily solved to get the $C_2O_4^{2-}$ concentration.

VI. Hydrolysis of Salts

RXN of a salt with water that leads to changes in pH.

A. Example - What happens to NaCN when it is dissolved in water?



Two reactions could possibly occur.



This reaction is no consequence since NaOH is a strong base and it would break apart to neutralize all the H^+ produced.



This is important because the HCN is a weak acid. Not all of the HCN would ionize and neutralize the hydroxide produced. The net effect of these reactions is to produce a basic solution.

This same type of analysis could be used for acidic salts such as NH_4Cl . The general rules are:

- 1. When a salt contains an anion or cation of a strong base (SB) or strong acid (SA), hydrolysis does not occur because it would give the SB or SA which would immediately dissociate.**
- 2. When a salt contains an anion or cation of a WA or WB, hydrolysis does occur because it gives a WA or WB which does not immediately dissociate.**

Thus

SA + SB \rightarrow salt which is neutral

SA + WB \rightarrow salt which is acid

WA + WB \rightarrow salt which is basic

WA + WB \rightarrow salt which is acid, basic or neutral

B. The hydrolysis constant - a special K_a or K_b .

Example - What is the pH of a 0.015 M NaCN solution?

Answer: pH = 10.8

- **The K_h for the CN^- may not be tabulated. In this case the K_h is a special K_b . We can show that**

$$K_a K_h = K_w$$

where K_a is the acid dissociation constant for HCN.

- **For the hydrolysis of a cation (example NH_4^+) from a weak base the hydrolysis constant will be a K_a and**

$$K_b K_h = K_w$$

where K_b is the base dissociation constant for NH_3 (in the hydrolysis of NH_4^+ example)

VII. Buffers

- A. Buffers are solutions which resist a change in pH. They are composed of a weak acid or weak base and the salt of the acid or base. Weak acid/salt buffers are acidic; weak base/salt buffers are basic.**

Main idea - The salt of a weak acid acts like a weak base.

The salt of a weak base acts like a weak acid. If the concentrations of weak acid/base and salt are fairly large then any added H^+ or OH^- will be absorbed without much change in pH.



- B. A useful expression for buffers is obtained by rearranging the weak acid or weak base ionization expression.**

$$pK_a = pH - \log_{10} ([A^-]/[HA]) \text{ and}$$

$$\text{pK}_b = \text{pOH} - \log_{10} \left(\frac{[\text{BH}^+]}{[\text{B}]} \right)$$

These equations are called the Henderson - Hasselbalch equations. Let's see how they can be applied.

- **From these equations it is easily seen that to get an acidic buffer of a particular pH, choose an acid with a pK_a close to the desired pH. To get a basic buffer choose a weak base with a pK_b close to the desired pOH.**
- **Example: What is the pH of a buffer formed by adding solutions of formic acid and sodium formate until the final concentrations are $[\text{HFor}] = .50 \text{ M}$ and $[\text{For}^-] = .70 \text{ M}$?**

Answer: 3.89

- **Example: What is the pH after adding 10.0 ml of 1.00 M HCl to the buffer above?**

Answer: 3.86

VIII. Titrations

A. A volumetric experimental technique for determining quantitative info about a substance.

- **In acid/base titrations the net result is**



The hydronium ions come from either strong or weak acid and the hydroxides come from either strong or weak base.

- **From stoichiometry we know that**

$$\text{moles added H}_3\text{O}^+ = \text{moles added OH}^-$$

so	$M_A V_A (\#\text{H}^+) = M_B V_B (\#\text{OH}^-)$
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This is called the equivalence point. Since we are making a salt in this reaction the equivalence point may be acid, basic, or neutral from the salt hydrolysis.

- We often use indicators to show when we reach the equivalence point. These indicators are weak organic acids or bases that change color in different pH solution. The indicator is picked depending on the salt produced by the titration. The indicator needs to change color in the pH range at the equivalence point.

Examples: What possible indicators could you use in a titration of ammonia and hydrochloric acid?

What possible indicators could you use for the titration of acetic acid with sodium hydroxide?

B. Classes of acid/base titrations

1. Strong base added to strong acid

This titration is neutral (pH 7) at the equivalence point.

- **To calculate the pH below the equivalence point.**

$$[\text{H}_3\text{O}^+] = \frac{\text{original moles H}^+ - \text{moles OH}^- \text{ added}}{\text{volume acid} + \text{total volume base}}$$

Example: What is the pH when you add 40. ml of 0.100 M NaOH to 50.0 ml of 0.100 M HCl?

- **At the equivalence point the pH is 7**
- **After the equivalence point there is no longer any acid to neutralize so $[\text{OH}^-] = [\text{excess base}]$**

$$[\text{OH}^-] = \frac{\text{total moles OH}^- - \text{original moles H}^+}{\text{volume acid} + \text{volume base}}$$

Important - If you add acid to base instead of base to acid the equations are reversed but the idea is the same - calculate the net concentration of hydroxide or hydronium in the solution and obtain the pH

2. Strong base added to weak acid

The solution is basic at the equivalence point.

- Before the equivalence point is reached use the Henderson/Hasselbalch equation

$$\text{pK}_a = \text{pH} - \log_{10} ([\text{A}^-]/[\text{HA}])$$

$$[\text{HA}] = \frac{\text{original moles HA} - \text{moles OH}^- \text{ added}}{\text{volume acid} + \text{total volume base}}$$

$$[\text{A}^-] = \frac{\text{total moles OH}^- \text{ added}}{\text{volume acid} + \text{volume base}}$$

Example: What is the pH after 20.0 ml of 0.100 M NaOH is added to 50.0 ml of acetic acid?

- At the equivalence point you have a solution of a basic salt. Find the concentration of salt produced and calculate as we have before.

- After the equivalence point there is no longer any acid to neutralize so $[\text{OH}^-] = [\text{excess base}]$

$$[\text{OH}^-] = \frac{\text{total moles added OH}^- - \text{original moles H}^+}{\text{volume acid} + \text{volume base}}$$

3. Strong acid added to weak base

The solution is acid at the equivalence point.

- Before the equivalence point is reached use the Henderson/Hasselbalch equation

$$\text{pK}_b = \text{pOH} - \log_{10} \left(\frac{[\text{BH}^+]}{[\text{B}]} \right)$$

$$[\text{B}] = \frac{\text{original moles B} - \text{moles H}^+ \text{ added}}{\text{volume acid} + \text{total volume base}}$$

$$[\text{BH}^+] = \frac{\text{total moles H}^+ \text{ added}}{\text{volume acid} + \text{volume base}}$$

- **At the equivalence point you have a solution of a acid salt. Find the concentration of salt produced and calculate as we have before.**
- **After the equivalence point there is no longer any base to neutralize so $[\text{H}^+] = [\text{excess acid}]$**

$$[\text{H}^+] = \frac{\text{total moles H}^+ - \text{original moles OH}^-}{\text{volume acid} + \text{volume base}}$$