# Acid Base Calculations with Salts

## Anions

1. Anions of weak acids will react with water, i.e. will hydrolyze to a significant extent and produce OH- ions thus increasing the pH of the solution, i.e., are basic anions. Example:

$$CH_3CO_2^-(aq) + H_2O(l) \leftrightarrow CH_3CO_2H(aq) + OH^-(aq)$$

2. Anions of strong acids will not hydrolyze to a significant extent and will, therefore, have no effect on the pH, i.e., are neutral anions.

## Cations

1. Cations that yield weak bases and produce $H3O^+$ lower the pH of the solution, i.e., are acidic cations. (example: $NH_4^+(aq)$)

2. Cations that are small and highly charged and extensively hydrated undergo hydrolysis by the loss of H+ from the bonded water and lower the pH of the solution, i.e., are acidic cations. (Example: $Al^{3+}$ and $Fe^{3+}$)

3. Cations of the IA family and the larger ions of the IIA family do not hydrolyze and will, therefore, have no effect on the pH, i.e., are neutral cations.

Definition of pKa :

(pK for short). The negative logarithm of the acid dissociation constant, Ka.

Just like the pH, the pKa tells you of the acid or basic properties of a substance.
pKa <2 means strong acid
pKa >2 but <7 means weak acid
pKa >7 but <10 means weak base
pKa >10 means strong base

**Acid Base Calculations with Salts**

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\left(\frac{[\text{conjugate base}]}{[\text{conjugate acid}]}\right)$$

$$= \mathrm{p}K_a + \log_{10}\left(\frac{[\text{proton acceptor}]}{[\text{proton donor}]}\right)$$

When dealing with weak acids and weak bases, you also might have to deal with the "common ion effect".

This is when you add a salt to a weak acid or base that contains one of the ions present in the acid or base.

To be able to use the same process to solve for pH when this occurs, all you need to change are your "start" numbers.

Add the molarity of the ion, which comes from the salt, and then solve the $\mathbf{K}_a$ or $\mathbf{K}_b$ equation as you did earlier.

# Question:

Find the pH of a .100 mol of $HC_2H_3O_2$ with a $K_a$ of 1.8 x $10^{-8}$ in a total volume of 1 Liter

## Answer:

$$HC_2H_3O_2(aq) \rightarrow H^+(aq) + C_2H_3O_2^-(aq)$$

# Question:

Find the pH of a .100 mol of $HC_2H_3O_2$ with a $K_a$ of $1.8 \times 10^{-8}$ in a total volume of 1 Liter

Now lets add a salt...we are going to add .200 moles of $NaC_2H_3O_2$

What are the parents of this salt?

Do you predict the pH to become more basic, acidic or remain the same? How would you know?

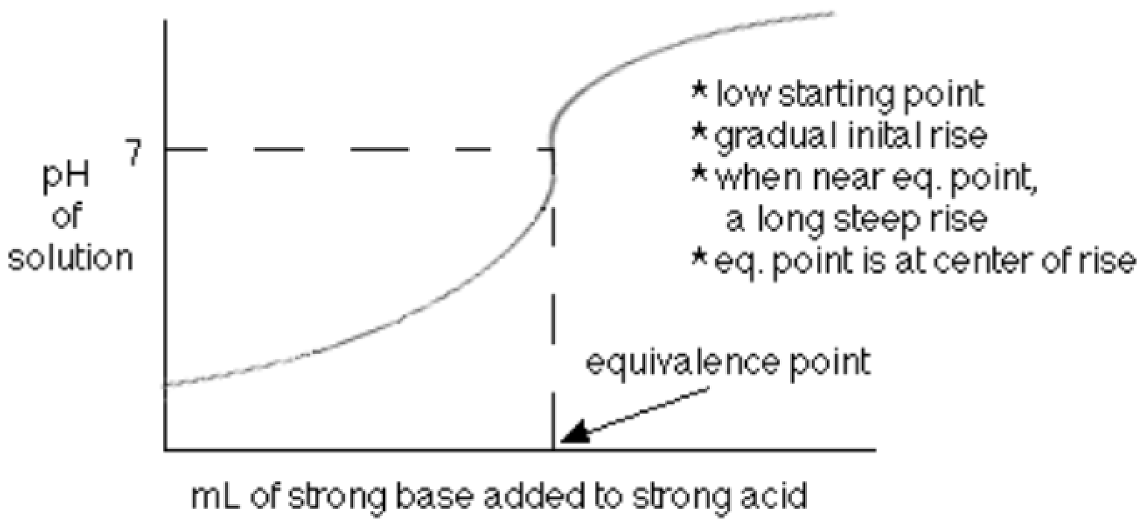
Note the common ion...all that does to your problem is....

**Answer:**

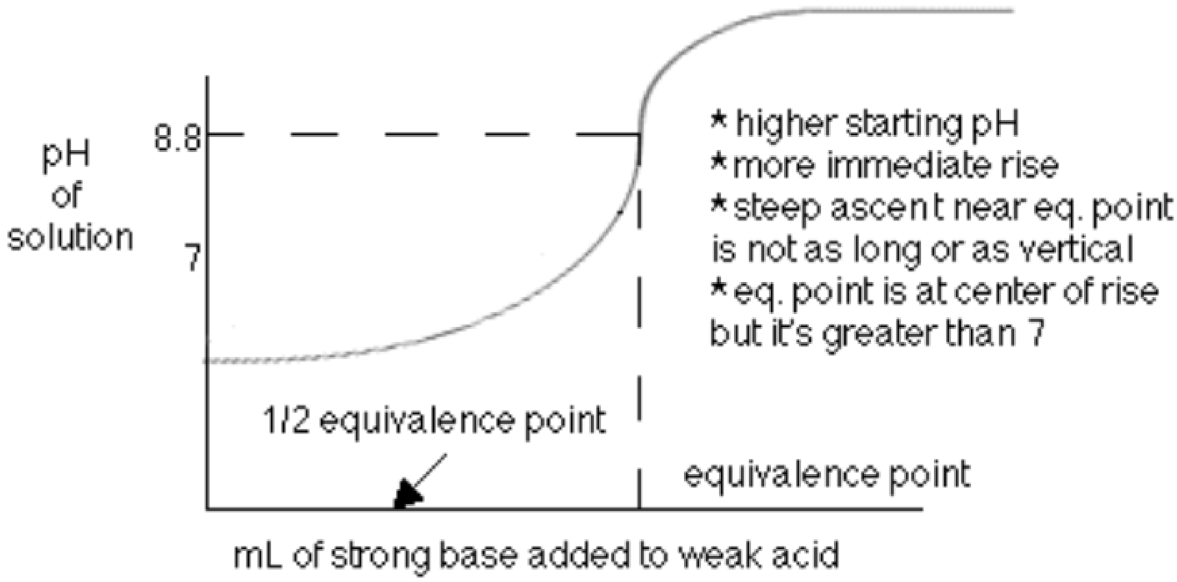
$$HC_2H_3O_2(aq) \rightarrow H^+(aq) + C_2H_3O_2^-(aq)$$

## Acid-Base Titrations

An acid-base titration is when you add a base to an acid until the equivalence point is reached which is where the number of moles of acid equals the number of moles of base. For the titration of a strong base and a strong acid, this equivalence point is reached when the pH of the solution is seven (7) as seen on the following titration curve:



For the titration of a strong base with a weak acid, the equivalence point is reached when the pH is greater than seven (7). The half equivalence point is when half of the total amount of base needed to neutralize the acid has been added. It is at this point where the pH = **p**$K_a$ of the weak acid.



In an acid-base titration, the base will react with the weak acid and form a solution that contains the weak acid and its conjugate base until the acid is completely gone. To solve these types of problems, we will use the $\mathbf{K_a}$ value of the weak acid and the molarities in a similar way as we have before. Before demonstrating this way, let us first examine a short cut, called the **Henderson-Hasselbalch Equation**.

This can only be used when you have some acid and some conjugate base in your solution.

If you only have acid, then you must do a pure $K_a$ problem and if you only have base (like when the titration is complete) then you must do a $K_b$ problem.

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

Where:

- pH is the log of the molar concentration of the hydrogen
- p$\mathbf{K_a}$ is the equilibrium dissociation constant for an acid
- [base] is the molar concentration of a basic solution
- [acid] is the molar concentration of an acidic solution

Example Problem:
25.0 mL of 0.400 M KOH is added to 100. mL of 0.150 M benzoic acid, $HC_7H_5O_2$ ($\mathbf{K}_a$=6.3x10$^{-5}$).
Determine the pH of the solution.

**Answer:**

Determine where in the titration we are:

0.400 M x 0.025 L = 0.0100 mol KOH added

0.150 M x 0.100 L = 0.0150 mol $HC_7H_5O_2$ originally

because only 0.100 mol of base has been added, that means the thitration is not complete; this means there are two ways to solve this problem: the normal way and the way using the Henderson-Hasselbalch Equation.

Normal way:

| | $HC_7H_5O_2$ + | $OH^-$ | $\leftrightarrow$ | $C_7H_5O_2^-$ + $H_2O$ | |
|---|---|---|---|---|---|
| before reaction: | 0.015 mol | 0.0100 mol | | 0 mol | -- |
| change: | -0.0100 | -0.0100 | | +0.0100 | -- |
| after reaction: | 0.0050 | 0 | | 0.0100 | -- |

$$K_a = \frac{[H^+][C_7H_5O_2^-]}{[HC_7H_5O_2]} = 6.3x10^{-5} = \frac{(x)(0.0100)}{0.0050}$$

$x = [H^+] = 3.2x10^{-5}$ M

pH = $-\log(3.2x10^{-5}) = 4.49$

Henderson-Hasselbalch Way:

$$[HC_7H_5O_2] = \frac{0.0050 \text{ mol}}{0.125 \text{ L}} = 0.040 \text{ M}$$

$$[C_7H_5O_2^-] = \frac{0.0100 \text{ mol}}{0.125 \text{ L}} = 0.0800 \text{ M}$$

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

$$pH = -\log(6.3\text{x}10^{-5}) + \log\frac{0.0800}{0.0400} = 4.20 + 0.30 = 4.50$$

This equation is used frequently when trying to find the pH of buffer solutions .

A buffer solution is one that resists changes in pH upon the addition of small amounts of an acid or a base.

They are made up of a conjugate acid-base pair such as $HC_2H_3O_2/C_2H_3O_2^-$ or $NH_4^+/NH_3$.

They work because the acidic species neutralize the $OH^-$ ions while the basic species neutralize the $H^+$ ions.

The buffer capacity is the amount of acid or base the buffer can neutralize before the pH begins to change to a significant degree. This depends on the amount of acid or base in the buffer. High buffering capacities come from solutions with high concentrations of the acid and the base and where these concentrations are similar in value.

## **Practice weak acid problem**:

$C_6H_5COONa$ is a salt of a weak acid $C_6H_5COOH$. A 0.10 M solution of $C_6H_5COONa$ has a pH of 8.60.

- Calculate $[OH^-]$ of $C_6H_5COONa$
- Calculate $\mathbf{K}_b$ for: $C_6H_5COO^- + H_2O <---> C_6H_5COOH + OH^-$
- Calculate $\mathbf{K}_a$ for $C_6H_5COOH$

**Solution:**

1) $14.00 - pH = pOH$ $\quad\quad$ $5.4 = -\log[OH^-]$

$14.00 - 8.60 = 5.4$ $\quad\quad$ $[OH^-] = 3.98 \times 10^{-6}$

2)

| | $C_6H_5COO^-$ | $\leftrightarrow$ | $C_6H_5COOH$ | + | $OH^-$ |
|---|---|---|---|---|---|
| Start | 10 M | | 0 M | | 0 M |
| Change | $-3.98x10^{-6}$ | | $+3.98x10^{-6}$ | | $3.98x10^{-6}$ |
| Equilibrium | $10-3.98x10^{-6}$ | | $3.98x10^{-6}$ | | $3.98x10^{-6}$ |

$$Kb = \frac{[C_6H_5COOH][OH^-]}{[C_6H_5COO^-]} = \frac{(3.98x10^{-6})(3.98x10^{-6})}{(.10 - 3.98x10^{-6})} = 1.6x10^{-10}$$

3) $Ka = \frac{Kw}{Kb} = \frac{1.00x10^{-14}}{1.6x10^{-10}} = 6.3x10^{-5}$

**Practice titration problem**:
20.00 mL of 0.160 M $HC_2H_3O_2$ ($\mathbf{K}_a$=1.8x$10^{-5}$) is titrated with 0.200 M NaOH.

- What is the pH of the solution before the titration begins?
- What is the pH after 8.00 mL of NaOH has been added?
- What is the pH at the equivalence point?
- What is the pH after 20.00 mL of NaOH has been added?

1) The titration hasn't started yet so this is just the standard Ka problem.

| | $HC_2H_3O_2$ | $\leftrightarrow$ | $H^+$ | + | $C_2H_3O_2^-$ |
|---|---|---|---|---|---|
| Start | 160 M | | 0 M | | 0 M |
| Change | -x | | +x | | +x |
| Equilibrium | 160-x | | x | | x |

$$Ka = 1.8x10^{-5} = \frac{(x)(x)}{.160 - x} \approx \frac{x^2}{.160}$$

$x = [H^+] = .0017$ M

pH = -log .0017 = 2.77

2) $.160 \text{ M x } .020 \text{ L} = .00320 \text{ mol } HC_2H_3O_2$ in solution

$.200 \text{ M x } .0080 \text{ L} = .0016 \text{ mol } NaOH$ added

We are in the middle of the titration. The .0016 mol of $NaOH$ will react with .0016 mol of $HC_2H_3O_2$ producing .0016 mol of the conjugate base, $C_2H_3O_2^-$, and leaving .0016 mol of $HC_2H_3O_2$. Because the solution has both the acid and the conjugate base, we can use the H-H equation.

$[HC_2H_3O_2] = \frac{.0016 \text{ mol}}{.028 \text{ L}} = .0571 \text{ M}$ $\quad$ $[C_2H_3O_2^-] = \frac{.0016 \text{ mol}}{.028 \text{ L}} = .0571 \text{ M}$

$\text{pH} = -\log 1.8\text{x}10^{-5} + \log\frac{.0571}{.0571} = 4.74$

3) At the equivalence point, the mols of $HC_2H_3O_2$ equals the mols of $NaOH$ (both are .0032 mol). All of the $NaOH$ reacts with all of the $HC_2H_3O_2$ to produce .0032 mol of $C_2H_3O_2^-$. Because there is no acid remaining, this is the standard Kb problem.

$\frac{.0032 \text{ mol}}{.200 \text{ M}}$ = .016 L of $NaOH$ must be added total to reach the eqpoint

$\frac{.0032 \text{ mol}}{.036 \text{ L}}$ = .089 M of $C_2H_3O_2^-$ is produced

| | $C_2H_3O_2^-$ | + $H_2O$ | $\leftrightarrow$ $HC_2H_3O_2$ | + $OH^-$ |
|---|---|---|---|---|
| Start | 089 M | -- | 0 M | 0 M |
| Change | - x | -- | + x | + x |
| Equilbrium | 089- x | -- | x | x |

$$Kb = \frac{Kw}{Ka} = \frac{1.00x10^{-14}}{1.8x10^{-5}} = 5.56x10^{-10}$$

$$Kb = 5.56x10^{-10} = \frac{(x)(x)}{.089 - x} \approx \frac{x^2}{.089}$$

$x = [OH^-] = 7.03x10^{-6}$ M

pOH = -log7.03x10$^{-6}$ = 5.15

pH = 14.00 − 5.15 = 8.85

4) We are past the equivalence point so this becomes an excess problem .

.200 M x .0200 L = .00400 mol NaOH added total

.0032 mol of NaOH will react with the 0032 mol of $HC_2H_3O_2$,

so there will be 000800 mol of NaOH remaining

$$[NaOH] = [OH^-] = \frac{.000800 \text{ mol}}{.040 \text{ L}} = .0200 \text{ M}$$