

Kvis

FUNDAMENTALS OF ACIDS AND BASES

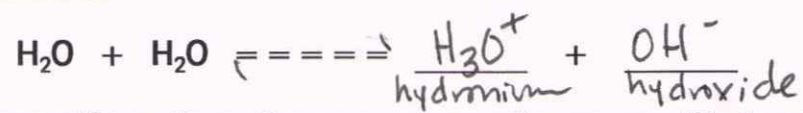
16.1-2 ^{1st} 2 pgs.

The Ionization of Water:

Water molecules react with each other, in pure form and in solution. This idea is known as autoionization.

Use note sheets for important intro topics or hand - They pay attention to me more & comprehend more - faster
** Highlighters*
** Circle eqns.*

The reaction is:



This is an equilibrium equation, therefore we can write an equilibrium expression for this reaction.

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

The molar concentration of water is a constant value and can be combined with the equilibrium constant to form a new constant, K_w .

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ (at } 25^\circ\text{C)}$$

or $[H^+][OH^-]$

Should be familiar

Recall that in a neutral solution $[H_3O^+]$ and $[OH^-]$ are equal.
Solve for these concentrations.

$$1 \times 10^{-14} = x^2 \qquad x = 1 \times 10^{-7}$$

When $[H_3O^+]$ is greater than $[OH^-]$, the solution is acidic.

When $[H_3O^+]$ is less than $[OH^-]$, the solution is basic.

Stress that as one conc. inc. the other dec. Refer back to eqn. & Lechat. inc. $[H_3O^+]$ shift left \therefore dec $[OH^-]$

Examples:

- When $[H_3O^+] = 3.90 \times 10^{-6}$,
a. What is $[OH^-]$? $(3.9 \times 10^{-6}) [OH^-] = 1 \times 10^{-14}$
 2.56×10^{-9}
b. Is the solution acidic, basic, or neutral?
 $H^+ > OH^-$ (acid)
- At 5°C , $K_w = 1.85 \times 10^{-15}$. If an aqueous solution has a $[H_3O^+] = 4.30 \times 10^{-8}\text{M}$, is the solution acidic, basic, or neutral?
solve for $[OH^-]$ $1.85 \times 10^{-15} = 4.3 \times 10^{-8} [OH^-]$ $[OH^-] = 4.3 \times 10^{-8}$
- Calculate the concentration of H^+ in a solution in which the hydroxide ion concentration is
a. $2.0 \times 10^{-5}\text{M}$ 5×10^{-10} **MB**
b. $4.0 \times 10^{-8}\text{M}$ 2.5×10^{-7} **MA**

The pH Concept:

Most solutions of weak acids and weak bases have small concentrations of H_3O^+ and OH^- . To allow for easy comparison between these concentrations and to make identification of a solution as acid, base, or neutral easier, a log system was developed called pH.

In general, the equation is: $pX = -\log X$

$pH = \frac{-\log [H^+]}{\text{also } [H_3O^+]}$ $pOH = \frac{-\log [OH^-]}{\text{also } [OH^-]}$

The pH scale is more common than the pOH scale, but pOH can be very useful in calculations. According to the pH scale:

$pH < 7$, acidic $pH = 7$, neutral $pH > 7$, basic

A useful relationship among pH, pOH, and pK_w can be derived from the equation for K_w .

$$pH + pOH = pK_w = 14$$

Examples:

- (1) Calculate the pH and pOH and determine whether acidic or basic.
 $[H_+] = 3.2 \times 10^{-5} M$ $pH = -\log 3.2 \times 10^{-5} = 4.5$ $pOH = 14 - 4.5 = 9.5$ acid
- $[OH^-] = 0.0026 M$ $pOH = 2.6$ $pH = 11.4$ base
- (2) When the $pH = 9.65$, what is the value of $[H_+]$?
 $9.65 = -\log [H^+]$ $[H^+] = 10^{-9.65} = 2.24 \times 10^{-10}$
- (3) An aqueous solution has a pOH of 10.00. $[H_+] = ?$ $pH = 4$ $4 = -\log [H^+]$ $[H^+] = 1 \times 10^{-4}$

The pH concept is rarely used for "strong" acids with concentrations greater than 1M. Why?

If $[H^+] = 2M$ $pH = -\log 2$ $pH = \ominus$

pH is just a scale to make comparison easier - no advantage to such pH's

We must now define "strong" acids or bases. The terms strong or weak do not refer to concentration, rather they refer to complete dissociation in water. Strong acids and bases therefore are not written as equilibrium equations.

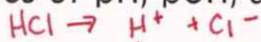
Strong acids: $H_2SO_4, HClO_4, HNO_3, HCl, HBr, HI$
 Strong bases: Group IA hydroxides, Group IIA hydroxides

Ask what does this mean?
 a dilute soln. of a strong acid

Example: Calculate the values of pH, pOH, and $[OH^-]$ for the following:

a. 0.020 M HCl

$[HCl] = .02$



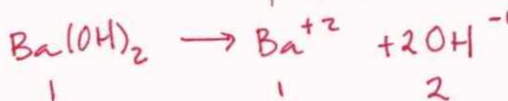
$-\log (.02) = pH = 1.7$ $[OH^-] = 5 \times 10^{-13}$
 $pOH = 12.3$

low [conc.] completely ionizes

b. 0.00035 M $Ba(OH)_2$

$[OH^-] = 2(.00035)$

$= .00070 M$



$pOH = 3.15$

$pH = 10.85$

from where? Water

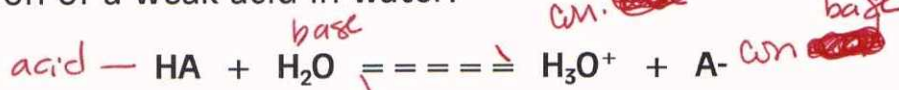
* single arrow

Ionization Constants for Weak Acids and Bases:

While strong acids and bases ionize completely, weak ones do not. They therefore exist in equilibrium with the ions formed by their reaction with water.

Ionization equation of a weak acid in water:

Bronsted acid donates proton



Since these reactions are in equilibrium, we can write an equilibrium equation for them.

General equation:
$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

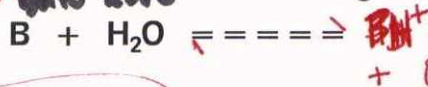
Ask them what's wrong with this equil expression

→ [H₂O] is constant

∴ combine K & [H₂O]

Ionization equation of a weak base in water:

Bronsted base accepts proton



acid (above K_a), *base* (below K_a)

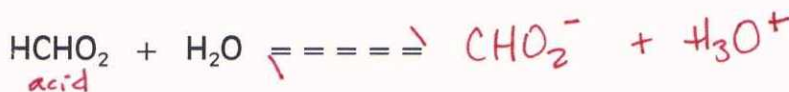
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

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

The value of K_a and K_b are usually small numbers and can be expressed in log form (like pH). $\text{p}K_a = -\log K_a$

The larger the K , the stronger the acid or base.
The larger the $\text{p}K_a$, the weaker the acid or base.

Write the ionization equation and equilibrium expression for the following:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]}$$

The resulting ion, CHO_2^- is a weak base in water and participates in the equilibrium.



$$K_b = \frac{[\text{HCHO}_2][\text{OH}^-]}{[\text{CHO}_2^-]}$$

There is an interesting relationship between the equilibrium constants for this acid-base pair.

$$K_a \times K_b = \left(\frac{[\text{H}_3\text{O}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]} \right) \left(\frac{[\text{HCHO}_2][\text{OH}^-]}{[\text{CHO}_2^-]} \right) = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

This relationship exists for any acid-base conjugate pair.

Because of this relationship, the following is also true:

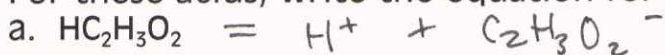
$$\text{p}K_a + \text{p}K_b = \text{p}K_w = 14$$

Tell them - this is an example used to derive

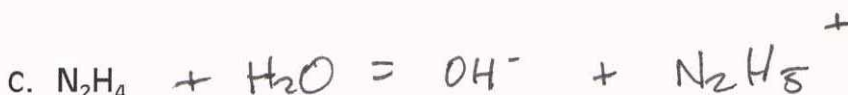
frust

Examples:

(1) For these acids, write the equation for the ionization reaction and the k_a .



(2) For these bases, write the ionization reaction and the k_b .



(3) What is the value of $\text{p}k_a$ for the bicarbonate ion if its k_a is 4.7×10^{-11} ?

10.33

$$\text{p}k_a = -\log 4.7 \times 10^{-11} = 10.32$$

(4) Which is the stronger acid, nitrous acid ($k_a = 7.1 \times 10^{-4}$) or formic acid ($k_a = 1.8 \times 10^{-4}$)? Defend your answer.

nitrous

larger $k_a = \text{stronger} = \text{nitrous}$

larger k means products are more abundant which means more ionization which is the measure

(5) Which is the stronger acid, HCN ($\text{p}k_a = 9.20$) or NH_4^+ ($\text{p}k_a = 9.24$)? of acid strength

HCN

(6) The k_b for the fluoride ion is 1.5×10^{-11} . What is its $\text{p}k_b$?

10.82

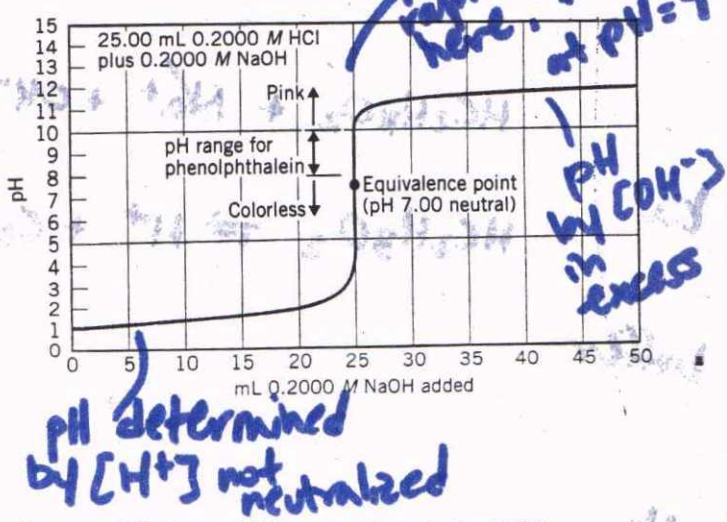
$$\text{p}k_b = -\log 1.5 \times 10^{-11}$$

$$\text{p}k_b = 10.82$$

Acid/Base Titrations

Titration of a Strong Acid by a Strong Base:

Consider what happens to the pH of 25 mL of 0.2 M HCl as it is titrated with 25 mL of 0.2 M NaOH. This result is shown in the diagram to the right. The diagram is referred to as a titration curve. As you add base, $[H^+]$ dec. and pH inc. until what happens? They become = pH=7
 $[OH^-] = [H^+]$
 This is the characteristic endpoint of a titration of a strong monoprotic acid with a strong base.



Example #1: The following quantities of 0.100 M NaOH have been added to 50.0 mL of 0.100 M HCl. Calculate the pH of the resulting solutions.

- a. 49.00 mL b. 50.00 mL c. 50.10 mL d. 51.00 mL

a) $? \text{ mol } H^+ = 50 \text{ mL} \left(\frac{1}{1000} \right) \left(\frac{.1 \text{ mol}}{1 \text{ L}} \right) = 5.00 \times 10^{-3} \text{ mol present}$

reacts with

$? \text{ mol } OH^- = 49 \times 10^{-3} \text{ L} \left(\frac{.1 \text{ mol}}{1 \text{ L}} \right) = 4.90 \times 10^{-3}$

All OH reacts

$\therefore H^+ \text{ left} = 5 \times 10^{-3} - 4.9 \times 10^{-3} = 1 \times 10^{-4} \text{ mol } H^+$
 $[H^+] = 1 \times 10^{-3} \text{ M}$
 $\{ \text{pH} = 3.00 \}$

b) $\text{mol } H^+ = \text{mol } OH^-$
 $\{ \text{pH} = 7 \}$

c) All H^+ reacts, OH^- in excess by .1 mL
 $? \text{ mol} = \frac{.1 \times 10^{-3} \text{ L}}{1} \left(\frac{.1 \text{ mol}}{1 \text{ L}} \right) = 1 \times 10^{-5} \text{ mol}$
 $\frac{1 \times 10^{-5} \text{ mol}}{100.1 \times 10^{-3} \text{ L}} = 9.99 \times 10^{-5} \text{ M} = [OH^-]$

$\text{pOH} = 4$
 $\text{pH} = 10$

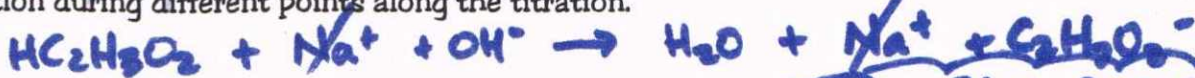
d) $\frac{1 \times 10^{-4} \text{ mol } OH^-}{101 \times 10^{-3} \text{ L}} = 9.9 \times 10^{-4} \text{ M}$
 $\text{pOH} = 3$

$\{ \text{pH} = 11 \}$

Because the pH change for strong/strong titrations is large near the equivalence point, the indicator would not change color at exactly pH = 7. Phenolphthalein is often the choice for strong/strong titrations. Its color change occurs during a pH change of 8.3 to 10, but just a slight excess (a few drops) of the titrant will cause this change

Titration of a Weak Acid with a Strong Base:

Consider the titration of acetic acid with sodium hydroxide. How can we calculate the pH of the acetic acid solution during different points along the titration.



$$K_a = \frac{[\text{C}_2\text{H}_3\text{O}_2^-][\text{H}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

1) Initially, the acetic acid is pure and can be calculated from



2) Before the equivalence point is reached, not all the available H has been neutralized. Before the pH can be calculated, we must determine what species are present so that we approach the problem from the correct perspective.

The equation shows that since both $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{C}_2\text{H}_3\text{O}_2^-$ are present, this becomes a buffer problem.

3) At the equivalence point, for a strong acid with a strong base, the pH = 7. This is not the case for a weak acid problem. Why? The other ions present are salts that contribute to the pH.

4) After the equivalence point has been reached, the additional OH^- has nothing left to react with so the pH is determined simply by $[\text{OH}^-]$ in excess.

list ions left - which have effect on pH? (weak)

Ex. #2 Twenty five mL of 0.200 M $\text{HC}_2\text{H}_3\text{O}_2$ is titrated with 0.200 M NaOH.

Since the molarities are equal and the acid is monoprotic, we will need 25 mL of NaOH to reach the equivalence point. Why is it important to realize this before we begin the problem?

1) What is the pH before titration?



$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{.2-x}$$

$$x = 1.9 \times 10^{-3} = [\text{H}^+]$$

pH = 2.72

not at pH=7 so we know how to approach the problem by the # ml NaOH added.

2) What is the pH after 10.00 mL of the base has been added?



| | | | |
|-------|--------------------|--------------------|--------------------|
| i | .143 | 0 | 0 |
| Δ | .143 | 0 | 0 |
| e | 2×10^{-3} | 2×10^{-3} | 0 |
| Final | 3×10^{-3} | 0 | 2×10^{-3} |

Use # moles
Convert to M by $\div 25 \times 10^{-3} \text{ L}$



$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+](5.71 \times 10^{-2})}{[8.57 \times 10^{-2}]}$$

$[8.57 \times 10^{-2}]$

or H.H. Egn.

$$[\text{H}^+] = 2.7 \times 10^{-5} \text{ M}$$

pH = 4.57

Use moles bc cancel out

salt conc

use H.H. Egn

Titration of a Weak Acid with a Strong Base:

Consider the titration of acetic acid with sodium hydroxide. How can we calculate the pH of the acetic acid solution during different points along the titration.



Ka

1) Initially, the acetic acid is pure and can be calculated from:



$$K_a = \frac{[\text{C}_2\text{H}_3\text{O}_2^-][\text{H}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

buffer

2) Before the equivalence point is reached, not all the available H has been neutralized. Before the pH can be calculated, we must determine what species are present so that we approach the problem from the correct perspective.

The equation shows that since both $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{C}_2\text{H}_3\text{O}_2^-$ are present, this becomes a buffer problem.

Salt

3) At the equivalence point, for a strong acid with a strong base, the pH = 7. This is not the case for a weak acid problem. Why? *The other ions present are salts that contribute to the pH.*

CONJ

4) After the equivalence point has been reached, the additional OH^- has nothing left to react with so the pH is determined simply by $[\text{OH}^-]$ in excess. *list ions left which have effect on pH (weak)*

Ex. #2 Twenty five mL of 0.200 M $\text{HC}_2\text{H}_3\text{O}_2$ is titrated with 0.200 M NaOH.

Since the molarities are equal and the acid is monoprotic, we will need 25 mL of NaOH to reach the equivalence point. Why is it important to realize this before we begin the problem?

1) What is the pH before titration?

not at pH=7

so we know how to approach the problem by the # mL NaOH added.



$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{.2 - x}$$

| | | | |
|---|------|----|----|
| i | .2 | 0 | 0 |
| Δ | -x | +x | +x |
| e | .2-x | x | x |

$$x = 1.9 \times 10^{-3} = [\text{H}^+]$$

pH = 2.72

USE H.E. EGN

2) What is the pH after 10.00 mL of the base has been added?

Use # moles



| | | | | |
|-------|---------------------|---------------------|---|--------------------|
| i | .143 | 0 | 0 | 0 |
| Δ | -2x10 ⁻³ | -2x10 ⁻³ | 0 | 2x10 ⁻³ |
| Final | 3x10 ⁻³ | 0 | 0 | 2x10 ⁻³ |

Convert to M. by ÷ 25x10⁻³ L

OR H.E. EGN.



$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+](5.71 \times 10^{-2})}{[8.57 \times 10^{-2}]}$$

$$[\text{H}^+] = 2.7 \times 10^{-5} \text{ M}$$

pH = 4.57

ok to use moles bc L cancel out

3) What is the pH when 25 mL of the base is added?

All H^+ reacts with all OH^- , Na^+ + $C_2H_3O_2^-$ left



$$\frac{5.0 \times 10^{-3} \text{ mol}}{50 \times 10^{-3} \text{ L}}$$

not effect on pH

$$K_b = 5.6 \times 10^{-10} = \frac{x^2}{.1}$$

$$x = 7.5 \times 10^{-6} = [OH^-]$$

$$pOH = 5.12$$

$$pH = 8.88$$

4) What is the pH after 26 mL of NaOH has been added?

25 mL reacts
1 mL left NaOH

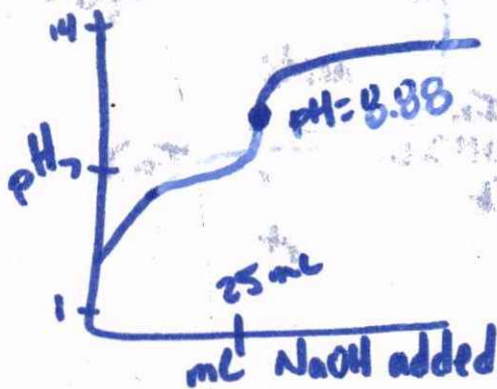
$$? \text{ mol } OH^- = \frac{1 \times 10^{-3} \text{ L}}{1} \left(\frac{.2 \text{ mol}}{1 \text{ L}} \right) = 2 \times 10^{-4} \text{ mol} / 51 \times 10^{-3} \text{ L}$$

$$= 3.92 \times 10^{-3} \text{ M } OH^-$$

$$pOH = 2.4$$

$$pH = 11.59$$

The titration curve for a weak acid with a strong base is similar to the curve for a strong acid with a strong base. Construct a titration curve for this problem and compare it to the curve for a strong/strong titration.



Eq. Point is higher (8.88 pH)
Beginning pH is higher bc weak acid

- (0, 2.72)
- (10, 4.57)
- (25, 8.88)
- (26, 11.59)

Conclusions for Titrations of Weak Acids:

1. The pH of a weak acid is higher initially than a strong acid of the same concentration because it is weak, less % ionization
2. The pH rises rapidly in the early part of a titration, but more slowly near the eq. point because it becomes an effective buffer near the eq. point.
3. The pH at equilibrium is not 7 because the resulting salt soln. the eq. point contributes to the pH.

