# Acid-Base Equilibrium

**See AqueousIons in Chemistry 121 On-line notes for review of acid-base fundamentals!**

Acid- Base Reaction in Aqueous Salt Solutions

Recall that use [ ] to mean "concentration of"
Recall that we will use $H^+$ and $H_3O^+$ interchangeably

| | | | |
|---|---|---|---|
| [H+] | = | [OH-] | neutral |
| [H+] | > | [OH-] | acid or acidic |
| [H+] | < | [OH-] | base or basic |

Naming Acids (below is review of 121 )

Binary acids

**Hydro………………ic acid**
**(nonmetal root)**

| | Compound | Aqueous solution |
|---|---|---|
| HCl | hydrogen chloride | hydrochloric acid |
| $H_2S$ | hydrogen sulfide | hydrosulfuric acid |
| HF | hydrogen fluoride | hydrofluoric acid |

Oxoacids

**………..ic acid**
**……….ous acid**
**(root)**

**ate → ic**
**ite → ous**

| | | |
|---|---|---|
| $SO_4^{2-}$ | Sulfate | |
| $H_2SO_4$ | hydrogen sulfate | sulfuric acid |
| $H_2SO_3$ | Hydrogen sulfite | sulfurous acid |
| $HNO_3$ | hydrogen nitrate | nitric acid |
| $HNO_2$ | hydrogen nitrite | nitrous acid |

If prefix continue to use:

| | |
|---|---|
| $HClO_4$ | perchloric acid |
| $HClO$ | hypochlorous acid |

Acid Salts

Use "bi" in place of hydrogen:

| | | |
|---|---|---|
| $HSO_4^-$ | hydrogen sulfate | bisulfate |

If several hydrogens then:

| | |
|---|---|
| $H_3PO_4$ | phosphoric acid |
| $H_2PO_3^-$ | dihydrogen phosphate |
| $HPO_3^{2-}$ | hydrogen phosphate |
| $PO_3^{3-}$ | phosphate |
| | |
| $NaHCO_3$ | sodium bicarbonate |
| ($Na^+$, $HCO_3^-$) | |

<u>Acids and Bases - Definitions</u>

Applications observed in lab:
Acid turns litmus red
Base turns litmus blue

| <u>Acid Base Concepts</u> | <u>Acid</u> | <u>Base</u> |
|---|---|---|
| **Arrhenius** | produce $H^+$, $H_3O^+$<br>hydronium | produce $OH^-$ in water<br>hydroxide |
| **Bronsted-Lowry** | donate proton | accept proton |
| **Lewis** | accept electron pair | donate electron pair |

Arrhenius Acids and Bases - Examples

Acid increase concentration of hydronium ion $H_3O^+$
Base increase concentration of hydroxide $OH^-$

| | | | | | | |
|---|---|---|---|---|---|---|
| Acid | HCl (aq) + | $H_2O$ | → | $H_3O^+$ (aq) | + | $Cl^-$ (aq) |
| | or write | HCl (aq) | → | $H^+$ (aq) | + | $Cl^-$ (aq) |
| | or write | HCl | → | $H^+$ | + | $Cl^-$ |
| Base | Ca $(OH)_2$ (s) | | → | $Ca^{2+}$ (aq) | + | $2OH^-$ (aq) |
| | $NH_3$ (aq) + | $H_2O$ | → | $NH_4^+$ (aq) | + | $OH^-$ (aq) |

Often combine acid to base or base to acid to neutralize the other
Acid + base → water + salt
HCl(aq) + NaOH(aq) → $H_2O$(l) + NaCl (aq) (stays as ions $Na^+$, $Cl^-$)

Bronsted-Lowry Examples

Acid is a substance that can donate a proton
Base is a substance that can accept a proton

Reaction involves transfer of proton from acid to base

| | | | | | | |
|---|---|---|---|---|---|---|
| Acid 1 | + | Base 2 | ⇔ | Acid 2 | + | Base 1 |
| $HC_2H_3O_2$ (aq) | + | $H_2O$ | ⇔ | $H_3O^+$ | + | $C_2H_3O_2^-$ |

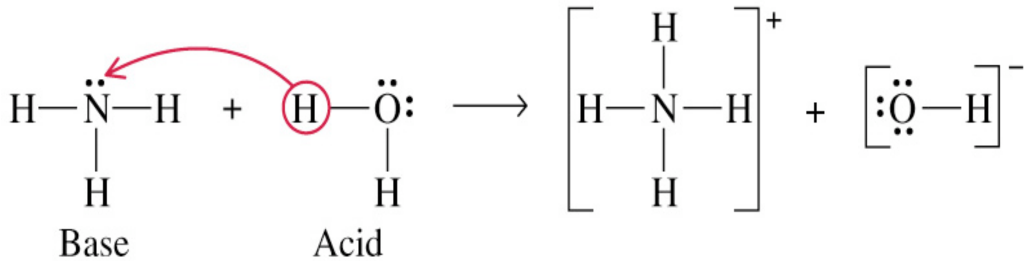
Conjugate acid base pairs (above):
Acid 1 to Base 1 - acid that gives up proton becomes a base
Base 2 to Acid 1 - base that accepts proton becomes an acid

Equilibrium lies more to left so $H_3O^+$ is stronger acid than acetic acid.

**Water can act as acid or base.**

| | | | | | | |
|---|---|---|---|---|---|---|
| Acid 1 | + | Base 2 | ⇔ | Acid 2 | + | Base 1 |
| $H_2O$ | + | $NH_3$ | ⇔ | $NH_4^+$ | + | $OH^-$ |

Conjugate acid base pairs (above):
Acid 1 to Base 1
Base 2 to Acid 1




http://cwx.prenhall.com/bookbind/pubbooks/hillchem3/medialib/media_portfolio/15.html

$NH_4^+$ is stronger acid than $H_2O$ ($NH_4^+$ wants to give up $H^+$)
$OH^-$ is stronger base than $NH_3$ ($OH^-$ want to get $H^+$)

When an acid gives up a proton it forms a base.
When a base accepts a proton if forms an acid.

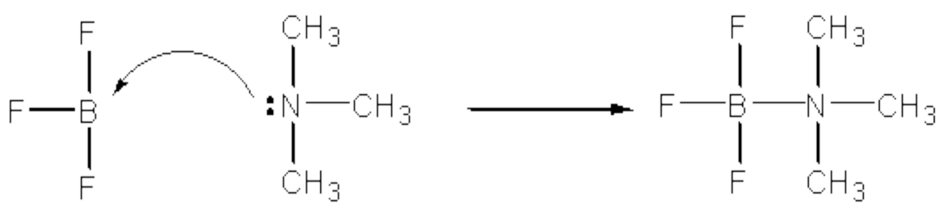
| | | | | | | |
|---|---|---|---|---|---|---|
| HA | + | $H_2O$ | ⇔ | $H_3O^+$ | + | $A^-$ |
| acid | + | base | | acid | | base |

Conjugate acid base pairs in blue and green.

Example

| | | | | | | |
|---|---|---|---|---|---|---|
| $NH_4^+$ | + | $H_2O$ | ⇔ | $H_3O^+$ | + | $NH_3$ |
| acid | | base | | acid | | base |

Lewis Acid-Base Reaction - Example (be aware of but we will not use much )



http://facultyfp.salisbury.edu/dfrieck/htdocs/212/rev/acidbase/lewis.htm

Definitions

Monoprotic- donate one proton (HCl, $HC_2H_3O_2$)

Polyprotic- can donate more than one proton

| | | | |
|---|---|---|---|
| $H_2SO_4$ | hydrogen sulfate | diprotic | sulfuric acid |
| $H_3PO_4$ | hydrogen phosphate | triprotic | phosphoric acid |

| | | | | | | |
|---|---|---|---|---|---|---|
| $H_2SO_4$ | + | $H_2O$ ⇔ | $H_3O^+$ | + | $HSO_4^-$ |
| $HSO_4^-$ | + | $H_2O$ ⇔ | $H_3O^+$ | + | $SO_4^{2-}$ |
| acid 1 | | base 1 | acid 2 | | base 1 |

Amphiprotic (or amphoteric) Ion or molecule than can accept or donate a proton.

Such as water OH- ← $H_2O$ → $H_3O^+$

Electrolytes – strong and weak

Electrolytes form ions in solution (conduct electricity).

**Strong electrolytes** completely ionize

**Weak electrolytes** partially ionize

Hydrochloric acid (**strong**)

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

Acetic acid (**weak**)

$HC_2H_3O_2$ (aq) + $H_2O$ (l) ⇔ $H_3O^+$ (aq) + $C_2H_3O_2^-$ (aq) Weak

Acetic acid stays mostly in the molecular form $HC_2H_3O_2$

and only small percent is in the ionic form $C_2H_3O_2^-$

Acid Equilibrium constant

Incorrect Form:

$$K = \frac{[H_3O^+]\,[C_2H_3O_2^-]}{[HC_2H_3O_2]\,[H_2O]}$$

Correct Form:

$$K = \frac{[H_3O^+]\,[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Pure liquids ($H_2O$) are not included in the equation

Do not include $H_2O$ because it is a pure liquid.

Normally write acid dissociation constant $K_a$

$$K_a = \frac{[H_3O^+]\,[C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{[H^+]\,[A^-]}{[HA]}$$

$\alpha$ = degree of dissociaton

fraction of molecule that is ionic form

100 $\alpha$= percent ionized

If $\alpha = 0.25$ then

25% ionized ($H^+$, $A^-$) and 75% unionized (HA)

Problems $K_a \Leftrightarrow$ concentration

1) **Find $K_a$ from concentrations**

Example:

At 25°C 0.100M acetic acid is 1.34% ionized. What is $K_a$?

98.66% unionized, 1.34% ionized

$$K_a = \frac{[H^+][HC_2H_3O_2^-]}{[HC_2H_3O_2^-]}$$

$[H+] = [C_2H_3O_2^-] = (0.0134)\,(0.1000) = 1.34\text{x}10^{-3}$ M (concentration)

$[HC_2H_3O_2^-] = (0.986)\,(0.1000) = 9.866\text{x}10^{-2}$ M (concentration)

$$K_a = \frac{(1.34\text{x}10^{-3})\,(1.34\text{ x}10^{-3})}{(9.87\text{x}10^{-2})} = 1.82\text{x}10^{-5}$$

In these problems, don't have to write units because concentration is always in M.

2) **Concentration of species in solution from $K_a$**

Of .10M $HNO_2$ (nitrous acid) $K_a = 4.5x10^{-4}$.

| | | | |
|---|---|---|---|
| $HNO_2$ ⇔ | $H^+$ | + | $NO_2^-$ |
| .10-x | x | | x |

Constant $K_a = \frac{[H^+]\,[NO_2^-]}{[HNO_2]}$

$4.5x10^{-4} = (x^2) / (0.10 – x)$

Simple approach:

If x is small (x < 5/100), then you do not need to use the quadratic equation because you can assume (0.10 –x) = 0.1 The variable x is so small that it will not make much difference in subtraction.

$4.5\ x10^{-5} = x^2$
$6.7\ x10^{-3} = x$

6.7% ionized and 93.3% unionized

Exact Solution:

$x^2 + 4.5\ x10^{-4}x – 4.5\ x10^{-5} = 0$

Quadratic Equation
$ax^2 + bx + c = 0$

Quadratic Formula for x
$x = \frac{-b \pm \sqrt{(b^2 - 4ac)}}{2a}$

Substitute in for a, b, c

$= \frac{-4.5\ x10^{-4} \pm \sqrt{((4.5\ x10^{-4})^2 – 4\ (1)\ (-4\ x10^{-5})}}{2\ (1)}$

$= \frac{-4.5\ x10^{-4} \pm \sqrt{(2.03\ x10^{-7} + 1.80\ x10^{-4})}}{2}$

$= \frac{-4.5\ x10^{-4} \pm 1.34\ x10^{-2}}{2}$

$= \frac{1.30 \times 10^{-2}}{2}$

$x = 6.5 \times 10^{-3}$ Select positive root, discard negative one (not shown)

$x = [H+] = [NO2-] = 6.5 \times 10^{-3}$ M .00065
$[HNO2] = 9.4 \times 10^{-2}$ M <u>.0935</u>
.0100

Percent Ionized
$(6.5 \times 10^{-3}/ 0.1) \times 100 = 6.5\%$ ionized
93.5% unionized

So to compare answers: approximate 6.7% exact 6.5%

Starts to be different above 5% but we will **simplify math if possible**

<u>Common calculator mistake</u>

If you want to enter this number $10^{-14}$ in calculator:
do 1E-14 which is $1 \times 10^{-14}$
NOT 10 E-14 which is the same as $10 \times 10^{-14}$

calculator takes E-14 to mean 10 raised to power -14
so
$10^3$ is 1E3
$10^{-4.5}$ is 1E-4.5
$3.2 \times 10^3$ is 3.2E3

However when you write numbers working problems **do not** use E in what you write
to put in calculator use 3.2E3 but for human to read write $3.2 \times 10^3$

Acid Strength

| | | | | |
|---|---|---|---|---|
| HA (aq) | + | $H_2O$ (l) ⇔ | $H_3O^+$ (aq) | + $A^-$ (aq) |
| Acid | | Base | Conjugate Acid | Conjugate Base |

With equilibrium expression
Acid dissociation constant: $\mathbf{K_a = \frac{[H^+]\,[A^-]}{[HA]}}$

| | | | |
|---|---|---|---|
| $K_a$ large | stronger acid | → favors right | goes to ionized form |
| $K_a$ small | weaker acid | ← favors left | stays unionized |

(molecular)

| | Acid Strength | Conjugate Base | |
|---|---|---|---|
| HCl | Stronger | Weaker | $Cl^-$ does not want proton<br>HCl → $H^+$ + $Cl^-$ |
| HCN | Weaker | Stronger | $CN^-$ wants proton HCN ← $CN^-$<br>HCN + $OH^-$ ← ⇔ $CN^-$ + $H_2O$ |

Strengths of Bronsted Acids and Bases

| | | | | |
|---|---|---|---|---|
| HA (aq) | + | $H_2O$ (l) ⇔ | $H_3O^+$ (aq) | + $A^-$ (aq) |
| Acid 1 | | Base 2 | Acid 2 | Base 1 |

HCl stronger acid than $H_3O^+$
$H_2O$ stronger base than $Cl^-$

Equilibrium favors weaker acid and weaker base
The stronger the acid the weaker the conjugate base

Tables available to relative strengths
For Example
HCl strong acid → $Cl^-$ weak base (does not want proton)
HCN weak acid → $CN^-$ strong base

Leveling Effect

Strongest acid that can exist in water is $H_3O^+$ so $HClO_4$, HCl, HBr, HCl, $HNO_3$, $H_2SO_4$ and other strong acids go completely to $H_3O^+$

Have to go to other solvent to deterimine order of strong acids
In $H_2O$, strongest base is $OH^-$

In water, strong acids (know these 6 common strong acids)

- HCl (hydrochloric)
- HBr (hydrobromic),
- HI (hydroiodic)
- $H_2SO_4$ (sulfuric)
- $HNO_3$ (nitric)
- $HClO_4$ (perchloric)

All of above are stronger than $H_3O^+$ but all produce $H_3O^+$

If solvent reduces different reagents to the same strength it is the **leveling effect**.
Water has leveling effect on bases stronger than $OH^-$

$NH_2^- + H_2O \rightarrow NH_3 + OH^-$
$NH_2^-$ is a strong base but $OH^-$ is the strongest base that can exist in water.

<u>Ionization of Water</u>

Water is a weak electrolyte

| | | | hydronium | | hydroxide |
|---|---|---|---|---|---|
| $H_2O$ | + | $H_2O \Leftrightarrow$ | $H_3O^+$ | + | $OH^-$ |
| | | $H_2O \Leftrightarrow$ | $H^+$ | + | $OH^-$ (aq) |

Bronsted Lowry
Acid: proton donor
Base: proton acceptor

Write $K_a$ for water

$$K_a = \frac{[H^+][OH^-]}{[H_2O]} \quad \text{or} \quad [H^+][OH^-]$$

$K_w = K_a$

$$\mathbf{K_w = 1.0 \times 10^{-14} = [H^+][OH^-]}$$

| In | | |
|---|---|---|
| | neutral solution | $[H^+] = [OH^-]$ |
| | acidic solution | $[H^+] > [OH^-]$ |
| | basic solution | $[H^+] < [OH^-]$ |

Example problems → given $H^+$ find $OH^-$

Given 0.020 M HCl solution
Find $[H^+]$ =? , $[OH^-]$ =?

| | HCl ⇔ | $H^+$ | + | $Cl^-$ |
|---|---|---|---|---|
| Initial | .020 | 0 | | 0 |
| Final | 0 | .020 | | .020 |

Strong electrolyte, contribution of neutral water is negligible
$[H^+] = .020$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = \frac{1.0 \times 10^{-14}}{0.2 \times 10^{-1}} = 5.0 \times 10^{-13}$$

$[OH^-] = 5.0 \times 10^{-13}$

40 billion $H^+$ for each $OH^-$ ion
50 water molecules for each $H^+$
2000 billion water molecules for each $OH^-$ ion

pH

negative log of hydrogen ion concentration, convenient way to represent concentration of $H^+$ ion

**$pH = -\log [H^+]$**

| pH | $[H^+]$ | $[OH^-]$ | |
|---|---|---|---|
| 14 | $10^{-14}$ | $10^{0}$ | basic, alkaline pH>7 |
| 10 | $10^{-10}$ | $10^{-4}$ | |
| 4 | $10^{-4}$ | $10^{-10}$ | |
| 0 | $10^{0} = 1$ | $10^{-14}$ | acidic pH<7 |

**$pOH = -\log [OH^-]$**

$[H^+]\,[OH^-] = 10^{-14}$
$\log [H^+] + \log [OH^-] = -14$

**$pH + pOH = 14$**

**$[H^+]\,[OH^-] = 1.0 \times 10^{-14}$**

**Connections using above equations**
**pH ⇔ $[H^+]$ ⇔ $[OH^-]$ ⇔ pOH ⇔ pH**

Example pH and pOH problems

1. Given $[H^+]$ Find pH
2. Given pOH Find $[H^+]$

Example 1

Given 0.020 M $H^+$, Find pH

$pH = -\log [H^+]$
$= -\log (0.020)$
$= -\log (2.0 \times 10\text{-}2)$
$= - [\log 2.0 + \log 10\text{-}2]$
$= - [ 0.301 + -2.00]$

pH =1.699 = 1.70 2 significant figures (remember pH is a logarithm)

Example 2

Given pOH = 4.40 Find $[H^+]$

pH = 14 – pOH = 14 - 4.40 = 9.60

$pH = -\log [H^+] \rightarrow [H^+] = 10^{-pH}$ antilog (pH)

$[H+] = 10^{-9.60} = 10^{-10} \times 10^{0.40}$ antilog (0.40) = 2.5
$= 2.5 \times 10^{-10}$

Logarithms and significant figures:

Form of logarithm such as 1.70 is characteristic.mantissa
In 1.70 the characteristic is the 1 which only holds the decimal place and the mantissa is the .70 the numbers after the decimal place.
Only the mantissa .70 is counted as sig figs

$10^{0.21} = 1.62$

2 sig fig if logarithm

1.21
12.21 → all 2 sig figs
0.21

Make sure on Calculator you are familiar with needed operations

$10^x$ or $y^x$ or log or inv log

log is base 10 common logarithm log (254) = 2.405
ln is base e (e=2.71828..) natural logarithm ln (254) = 5.537
Remember pH and POH use common logarithms (log)

Indicators and Equilibrium

Measure pH with pH meter where response of meter depends on $[H^+]$ concentration
More qualitative is the use of indicators

Indicator- organic compounds whose color depends on $[H^+]$ concentration of solution

| | | | |
|---|---|---|---|
| litmus | red | pH < 5 | HIn litmus molecule |
| litmus | purple | pH = 5–8 | |
| | blue | pH > 8 | $In^-$ litmus ion |

$$HIn \Leftrightarrow H^+ + In^-$$

Red blue

increase $H^+$ acid then shift to left side (turns red)
add OH- which decreases $H^+$ then shift to right side (turns blue)

Litmus has $K_a$ value $= 10^{-7} = \frac{[H^+][In^-]}{[HIn]}$

so

$\frac{10^{-7}}{10^{-5}} = \frac{[In^-]}{[HIn]} = \frac{1}{100}$ Requires 100x more HIn than $In^-$ to appear red

$\frac{10^{-7}}{10^{-8}} = \frac{[In^-]}{[HIn]} = \frac{10}{1}$ Requires 10x more $In^-$ than HIn to appear blue

Demo: Bromocreosol green indicator

$HIn \Leftrightarrow H^+ + In^-$
green — blue

add acid $H^+$ then shifts to left and turns green

add base $OH^-$ removes H+ then shifts to right and turns blue

Base Equilibrium

$\mathbf{K_a K_b = K_w}$

$\mathbf{K_b = \frac{[HA][OH^-]}{[A^-]}}$ $\mathbf{A^- + H_2O \Leftrightarrow HA + OH^-}$

$K_a = \frac{[H^+][A^-]}{[HA]}$ $HA \Leftrightarrow H^+ + A^-$

$K_aK_b = \frac{[H^+][A^-]}{[HA]}\frac{[HA][OH^-]}{[A^-]}$

$K_aK_b = [H^+][OH^-] = K_w$

and since $Kw = 1.0x10^{-14}$ then

$\mathbf{K_a K_b = 1.0\ x10^{-14}}$

example for HCN and $CN^-$
$K_a$ (HCN) = 4.9 $x10^{-10}$
$K_b$ (CN-) = 2.04 $x10^{-5}$

and $K_a K_b = 1.0\ x10^{-14}$

What is the pH if concentration of ion and acid are equal?

$K_a = [H^+][C_2H_3O_2^-] / [HC_2H_3O_2]$

if $[C_2H_3O_2^-] = [HC_2H_3O_2]$ then

$K_a = [H^+]$ $K_a$ available Table in textbook so can define **pKa = -log $K_a$**

So
**pH = $pK_a$** if [acid] = [conjugate base ion] one way to make buffer

pH will begin to change if too much acid or base added

if [acid] = [ion] = 1.00 M then
Add 0.01 mol of strong acid or base in 1L of solution with buffer to begin to change pH of buffer solution

Basic Buffer

**pOH = $pK_b$**

Buffer

A solution that has a constant pH when small amounts of acid or base are added
A solution that resists changes in pH

| Type of buffer | need equal concentration |
|---|---|
| acidic, low pH | weak acid and salt with common anion |
| basic, high pH | weak base and salt with common cation |

Acid buffer:

| | | | |
|---|---|---|---|
| $HC_2H_3O_2$ | acetic acid | $H^+$ | $C_2H_3O_2^-$ |
| $NaC_2H_3O_2$ | sodium acetate | $Na^+$ | $C_2H_3O_2^-$ |

$HC_2H_3O_2 \Leftrightarrow H^+ + C_2H_3O_2^-$ $\quad K_a = 1.8 \times 10^{-5}$
1.0M $\quad$ $1.8 \times 10^{-5}$ $\quad$ 1.0M
remove $H^+$ (shift → to replenish
added $H^+$ (shift ← to use up)

Basic buffer:

add equal amounts of

| | | | |
|---|---|---|---|
| $NH_3$ | ammonium | $NH_4^+$ and | $OH^-$ |
| $NH_4Cl$ | ammonium chloride | $NH_4^+$ and | $Cl^-$ |

$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$ $\quad K_b = 1.8 \times 10^{-5}$
0.10 $\quad$ 0.10 $\quad$ 1.8 x10-5
remove $OH^-$ (shift → to replace)
added $OH^-$ (shift ← to remove)

$K_a (NH_4^+) = 5.56 \times 10^{-10}$

Example Buffer:

Acetic acid and acetate buffer $Ka = 1.82 \times 10^{-5}$

$pH = 4.740$

Equal amounts $pH = pK_a$

$$HC_2H_3O_2 \Leftrightarrow H^+ + C_2H_3O_2^-$$

| $HC_2H_3O_2$ | $H^+$ | $C_2H_3O_2^-$ |
|---|---|---|
| 1.00 | $1.82 \times 10^{-5}$ | 1.00 mol/L |

What is pH after 0.010 OH- is added?

$$K_a = \frac{[H^+]\,[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

Initial $[H^+] = 1.82 \times 10^{-5}$ and pH= 4.740

| pH (w/o buff) | OH- added | $HC_2H_3O_2 \Leftrightarrow$ | $H^+$ | + | $C_2H_3O_2^-$ | pH (with buffer) |
|---|---|---|---|---|---|---|
| | | 1.00 | | | 1.00 | 4.740 |
| 11 | 0.001 | 0.999 | | | 1.001 | 4.74 |
| 12 | 0.01 | 0.990 | | | 1.01 | 4.75 |
| 13 | 0.1 | 0.90 | | | 1.1 | 4.85 |

$$Ka = \frac{[H^+]\,(1.1)}{(0.9)}$$

$$1.82 \times 10^{-5} = \frac{[H^+]\,(1.1)}{(0.9)}$$

$[H^+] = 1.49 \times 10^{-5}$

$pH = -\log [H^+] = -\log (1.49 \times 10^{-5})$

$pH = 4.83$

Review alkaline or acid buffer

1/1 ratio where $pH= pK_b$ or $pH = pK_a$

What if ratio other than 1/1 used what will pH be?

**Henderson Haselbalch Equation**

$$\mathbf{pH = pK_a + \log \frac{[A^-]}{[HA]}}$$

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} \qquad HA \Leftrightarrow H^+ + A^-$$

$$[H^+] = (K_a)\,\frac{[HA]}{[A^-]}$$

$$\log [H^+] = \log K_a + \log \frac{[HA]}{[A^-]}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

Range of ratios 1/10 to 10/1
log (1/10) = -1 and log (10/1) =1

$pH = pK_a \pm 1$ Can select range if not too far from $pK_a$

Buffer:

| | | | |
|---|---|---|---|
| $HC_2H_3O_2$ ⇔ | $H^+$ | + $C_2H_3O_2^-$ | $Ka = 1.82 \times 10^{-5}$ |
| 1.0 | | 1.00 mol/L | |

0.1 OH- base neutralizes some of acid

| | |
|---|---|
| 0.9 | 1.1 |

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

$$[H^+] = K_a \frac{[HC_2H_3O_2]}{[C_2H_3O_2^-]}$$

$$[H^+] = (1.82 \times 10^{-5})(0.9/1.1)$$
$$= 1.49 \times 10^{-5}$$

pH = 4.83

No Buffer:

Compare to 0.01M NaOH to pure water

$pOH = -\log [OH^-]$
$= -\log (.01) = 2$ → pH = 12

pH change from 7 → 12
for buffer change from 4.74 → 4.749

Buffer – another example

Cyanic acid- cyanate buffer to set pH = 3.5
What concentrations?

$HOCN \Leftrightarrow H^+ + OCN^-$

$$K_a = 1.2 \times 10^{-4} = \frac{[H^+]\,[OCN^-]}{[HOCN]}$$

With Henderson- Haselbalch Eq.:

$$pH = pK_a + \log \frac{[OCN^-]}{[HOCN]}$$

$3.50 = 3.92 + \log x$

$-0.42 = \log x$

$$10^{-0.42} = 0.38 = \frac{[OCN^-]}{[HOCN]}$$

$[OCN^-] = 0.38$ M

$[HOCN] = 1.00$M

Without Henderson- Haselbalch Eq.:

$10^{-pH} = [H^+] = 10^{-3.5} = 3.16 \times 10^{-4}$
or pH = 3.5

$$K_a = \frac{[H^+]\,[OCN^-]}{[HOCN]}$$

$$\frac{Ka}{[H^+]} = \frac{1.2 \times 10^{-4}}{3.16 \times 10^{-4}} = \frac{[OCN^-]}{[HOCN]} = 0.38$$

$[OCN^-] / [HOCN] = 0.38$ so

could have $[OCN^-] = 0.38$ M and $[HOCN] = 1.00$M

Mixing (cation) (anion) ions in water and effect

1. Neither cation or anion acts as acid or base.
   Cation of strong base $Li^+$, $K^+$, $Na^+$, $Ba^{2+}$, $Sr^{2+}$
   Anion of strong acid $Cl^-$, $NO_3^-$, $SO_4^{2-}$
   Results of Mixing cation and anion: Neutral

2. Cation is acid. NH4$^+$
   Anion is weak base. $Cl^-$, $NO_3^-$
   Results of Mixing cation and anion: Acidic

3. Cation does not act as acid. $Na^+$, $Na^+$, $K^+$
   Anion acts as base. $CN^-$, $C_2H_3O_2^-$, $CO_3^{2-}$
   Results of Mixing cation and anion: Basic

4. Cation acts as acid. 1) $NH_4^+$, 2) $NH_4^+$
   Anion acts as base. 1) $C_2H_3O_2^-$, 2) $CO_3^{2-}$
   Results of Mixing cation and anion (1) : Acidic
   Results of Mixing cation and anion (2) : Basic

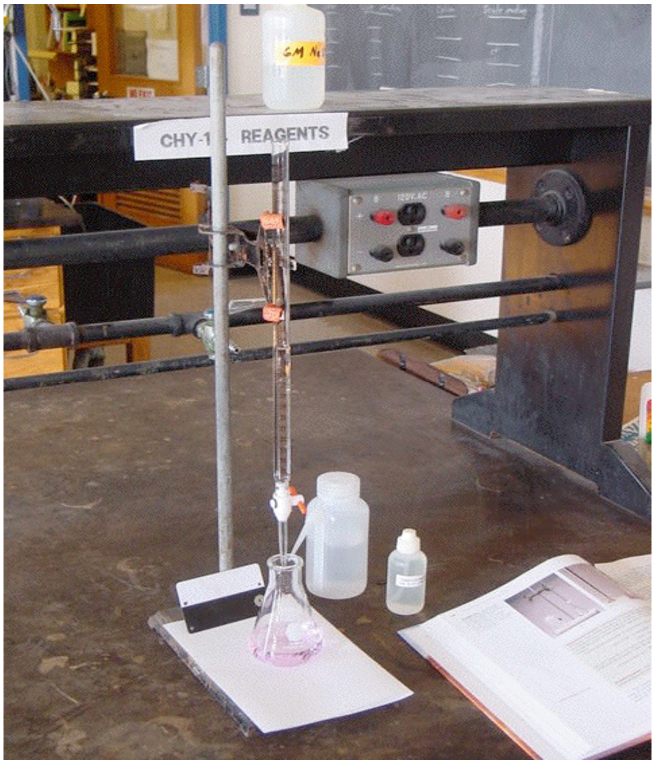
In case 4 have to know more information about acid and base such as $K_a$ and $K_b$ values. $K_a$ and $K_b$ are acid dissociation constant and base dissociation constant, respectively explained in chapter.

Chemical Analysis and Titrations

Refer to lab work of acid/ base
Use reaction to determine amounts

Familiar with terminology of titrations

Titrant
Buret
Indicator endpoint etc.
Acid base
Redox
Precipitation




http://images.google.com/imgres?imgurl=http://www.usm.maine.edu/chy/manuals/114/images/ABTitr01.gif&imgrefurl=http://www.usm.maine.edu/chy/manuals/114/text/ABTitr.html&h=640&w=480&sz=187&tbnid=V7NZN4ynP3m-WM:&tbnh=137&tbnw=103&hl=en&start=2&prev=/images%3Fq%3Dacid%2Bbase%2Btitration%26gbv%3D1%26svnum%3D10%26hl%3Den%26ie%3DUTF-8%26oe%3DISO-8859-1%26sa%3DG

Acid Base Titrations

1) Strong acid titrated with strong base

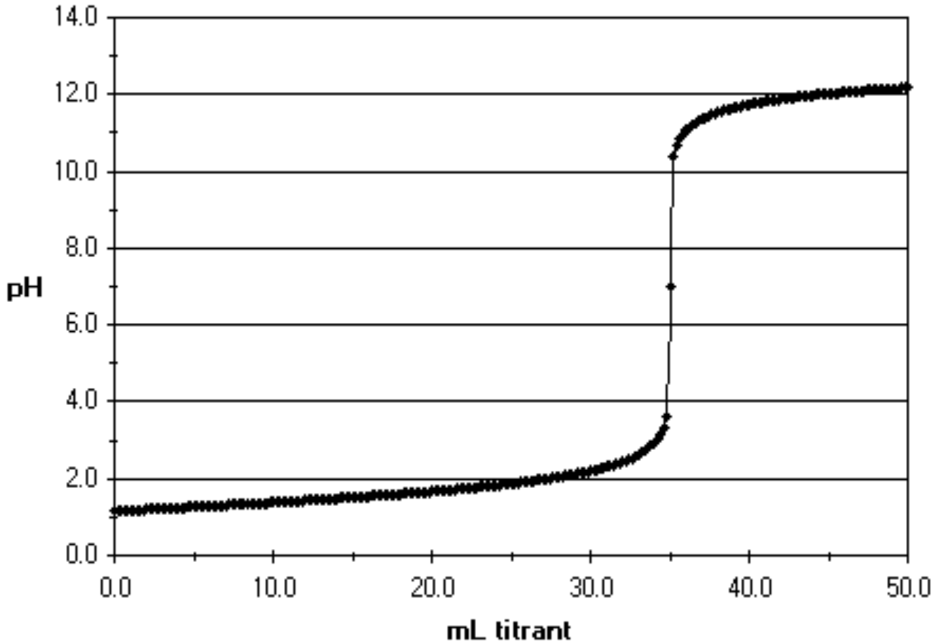
35 mL 0.1M HCl
pH = -log $[H^+]$
pH= 1.00

add 0.1 M NaOHto solution that has few drops of indicator in it

At equivalence point (35mL of base in example below) all the acid is neutralized. Equal moles of base ($OH^-$) have been added to cancel the original ($H^+$). pH is now 7.0

$$\mathbf{N_A V_A = N_B V_B}$$ Note: N= normality

or $$\mathbf{n_A M_A V_A = n_B M_B V_B}$$




http://www.chemicool.com/img1/graphics/titration-strong-acid-35ml.gif

2) Titrate weak acid with strong base

Suppose 50.0 mL of $HC_2H_3O_2$ 0.1M

$$Ka = 1.8 \times 10^{-5} = \frac{[H^+][A^-]}{[HA]}$$

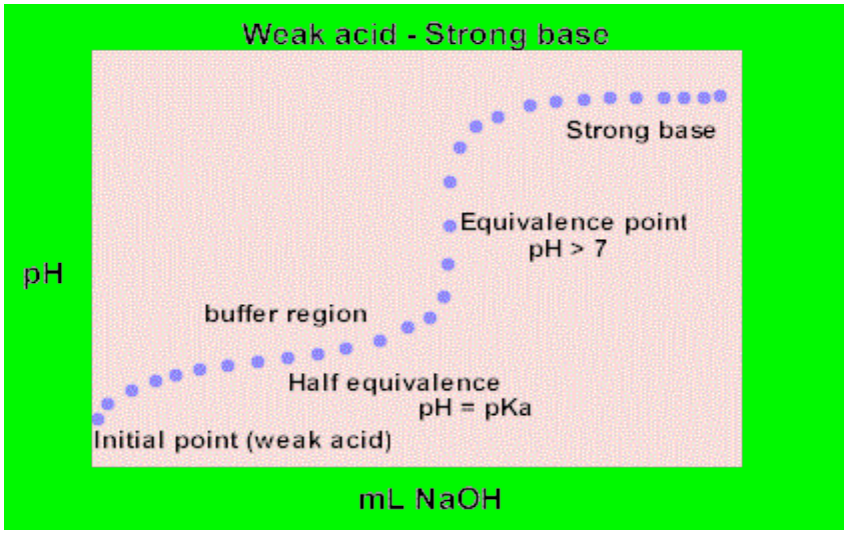
Initial pH

$1.8 \times 10^{-5} = x^2/ .1$

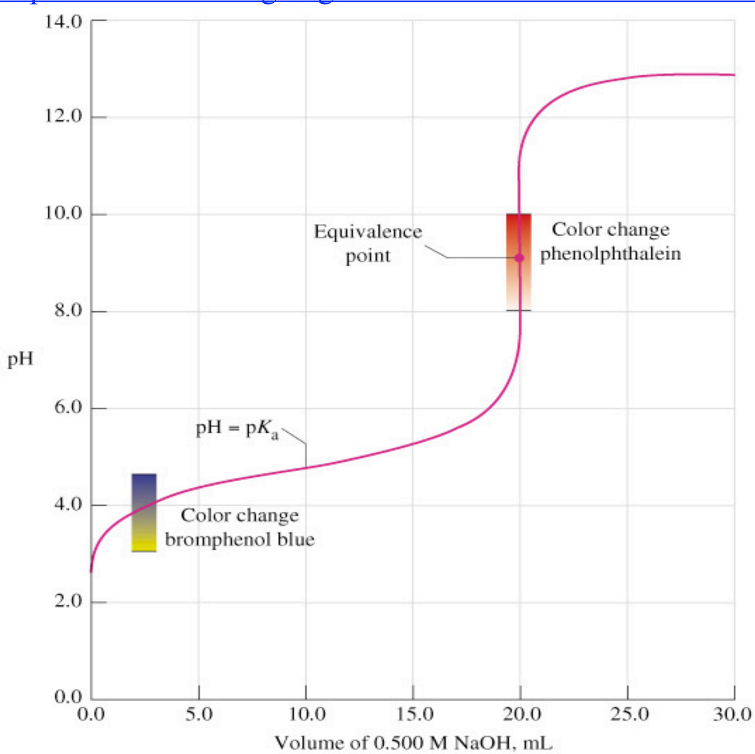
$1.8 \times 10^{-6} = x^2$

$1.34 \times 10^{-3} = [H+]$

pH = 2.87




http://bouman.chem.georgetown.edu/S02/lect19/lect19.htm




http://cwx.prenhall.com/bookbind/pubbooks/hillchem3/medialib/media_portfolio/15.html

pH begins above 1 because acid is only partially ionized

Note that at equivalence point pH > 7 since $C_2H_3O_2^-$ is anion of weak acid

$$C_2H_3O_2^- + H_2O \Leftrightarrow HC_2H_3O_2 + OH^-$$

Base

At equivalence point:
100% $C_2H_3O_2^-$, 0% $HC_2H_3O_2$

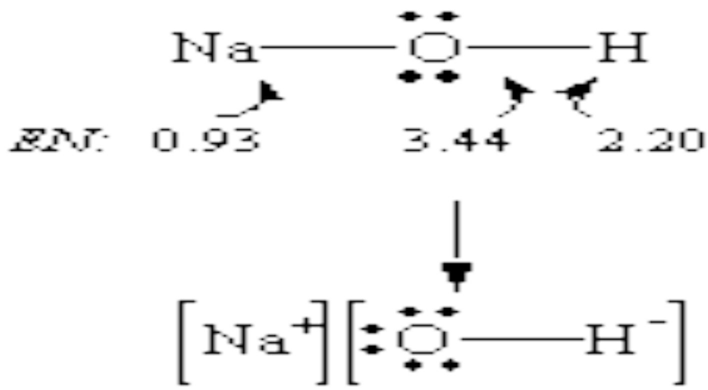
At 1/2 equivalence point:
50% $C_2H_3O_2^-$, 50% $HC_2H_3O_2$

Since $Ka = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$

Structures of Hydroxy Compounds

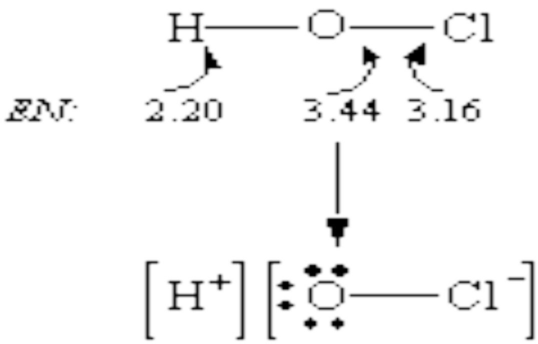
NaOH is base and HOCl is acid
Why different?

Low electronegativity tends to donate electrons to form positive species



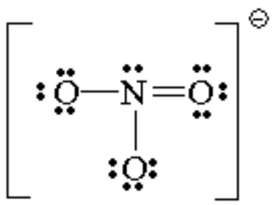

http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch11/acidbaseframe.html

High electronegativity tends to have a strong attraction for electrons so it removes electrons




http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch11/acidbaseframe.html

More oxygens means stronger. The acid oxygen atom helps to support removed charge.




http://wwwphys.murdoch.edu.au/teaching/chemtutorials/m140tests/test2mcqs12000.htm

Hydroxy compounds:
Metals low electronegativity yields $OH^-$ base
Nonmetals or metals with high oxidative numbers and high electronegativities yield $H^+$ in water.

Strengths and Structure of Acids

Hydrides are binary compounds
In periodic table, across the table going right and down goes towards stronger binary.

In period, increasing strength → goes to the right on table because higher electronegativity so withdraws electrons more and thus release proton.

Example:

| | | | | |
|---|---|---|---|---|
| N | < | O | < | F |
| $NH^3$ | | $H^2O$ | | HF |
| base | | neutral | | acid |

In group, larger size as you go down a group because large electron cloud allows electrons to be more easily removed.

Example acid strength:
HF < HCl < HBr < HI
Weak acids                Strong acids

Size dominates when going down a group.

Oxoacids

General Form:
  a    b
H - O - Z

If you go up the periodic table and across to the right then you will go towards stronger oxoacids. (Up group, right across period)

Example:

NaOH < HOH < HOCl

If Z metal with low electronegativity (Na) then pair b belong to O and acts as base $OH^-$.

If Z nonmetal then pair b is covalent bond and Z will tend to help reduce electron density even though O is electronegative.

Higher electronegativity of Z the easier protons are lost

HOI < HOBr < HOCl
Stronger acid
Electronegativity

If Oxygen around Z then they help to withdraw charge from the H-O bond

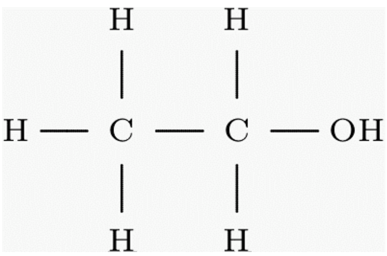
More oxygens then stronger the substance is as an acid

Oxygens not OH
$(HO)_mZO_n$

| n | | | | |
|---|---|---|---|---|
| | 0 | very weak acid | | HOCl |
| 1 | weak acid | HOClO | HONO | $(HO)_2SO$ |
| 2 | stronger acid | $HOClO_2$ | $HONO_2$ | $(HO)_2SO_2$ |
| 3 | very strong acid | $HOClO_3$ | | |

Remember not all hydrogens come off

Ethanol not acidic




http://july.fixedreference.org/en/20040724/wikipedia/Ethanol

As concentration decreased → Percent ionization increases

$HC_2H_3O_2 + H_2O \Leftrightarrow H_3O^+ + C_2H_3O_2^-$

Le Chatlier's Principle

to dilute you Increase water on left which causes shift to right and thus percent ionized increases

| Conc. | % Ionized |
|---|---|
| 1.0 | 0.43 |
| 0.01 | 4.18 |
| 0.001 | 12.6 |

**EXTRA STUFF BELOW Chem 122 can ignore**

Oxidizing and Reducing Agents

Don't expect to know all this but be able to use if given

3 most common

| Oxidizing Agent | Name | Color | Metal is reduced |
|---|---|---|---|
| $Mn^{+7}O_4^-$ | permanganate | purple | (+2) Mn |
| $Cr^{+6}O_4^{2-}$ | chromate | yellow- in base | (+3) Cr |
| $Cr_2^{+6}O_7^{2-}$ | dichromate | red- in acid | (+3)Cr |

Reducing Agents

Metal is oxidized to give up electron so something else oxidizes

Metals

Mg, Zn

$Zn \rightarrow Zn^{2+} + 2e^-$

Or metal ions (homogeneous solution)

$Sn^{2+}$ (aq) $\rightarrow$ $Sn^{4+}$ (aq) + $2e^-$

$Sn^{4+}$, metal is oxidized