Acid-Base Equilibrium

See AqueousIons in Chemistry 1110 online 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 CHEM 1110)

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
$NaHCO_3$ (Na^+, HCO_3^-)	sodium bicarbonate

Acids and Bases - Definitions

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

Acid Base Concepts	Acid	Base
Arrhenius	produce H^+, H_3O^+ hydronium	produce OH^- in water 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 $HCl\ (aq) + H_2O \rightarrow H_3O^+\ (aq) + Cl^-\ (aq)$

or write $HCl\ (aq) \rightarrow H^+\ (aq) + Cl^-\ (aq)$

or write $HCl \rightarrow H^+ + Cl^-$

Base $Ca(OH)_2\ (s) \rightarrow Ca^{2+}\ (aq) + 2OH^-\ (aq)$

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

Often combine acid to base or base to acid to neutralize the other
Acid + base → water + salt
$HCl(aq) + NaOH(aq) \rightarrow H_2O(l) + NaCl\ (aq)$ (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^+	+	$C_2H_3O_2^-$

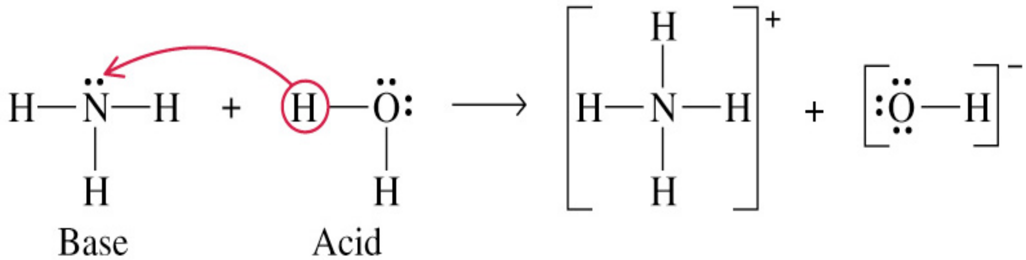
Conjugate acid base pairs (above):
Acid 1 to Base 1 - acid that gives up proton becomes a base
Base 2 to Acid 1 - base that accepts proton becomes an acid

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.

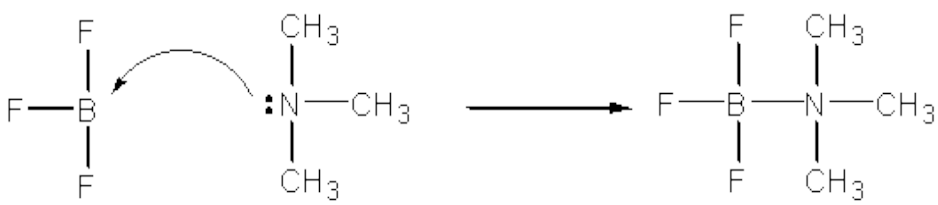
HA	+	H_2O	⇔	H_3O^+	+	A^-
acid	+	base		acid		base

Conjugate acid base pairs in blue and green.

Example

NH_4^+	+	H_2O	⇔	H_3O^+	+	NH_3
acid		base		acid		base

<u>Lewis Acid-Base Reaction - Example</u> (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 (weak acids)

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

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

α = degree of dissociaton
fraction of molecule that is ionic form

100 α= 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

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

$[H+] = [C_2H_3O_2^-] = (0.0134)\,(0.1000) = 1.34x10^{-3}$ M (concentration)
$[HC_2H_3O_2^-] = (0.986)\,(0.1000) = 9.866x10^{-2}$ M (concentration)

$$K_a = \frac{(1.34x10^{-3})\,(1.34\ x10^{-3})}{(9.87x10^{-2})} = 1.82x10^{-5}$$

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) = 0.10 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)

$x = [H+] = [NO_2-] = 6.5 \times 10^{-3}$ M .0065
$[HNO_2] = 9.4 \times 10^{-2}$ M .0935
.100

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**

Common calculator mistake

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

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

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)

	<u>Acid Strength</u>	<u>Conjugate Base</u>	
HCl	Stronger	Weaker	Cl^- does not want proton $HCl \rightarrow H^+ + Cl^-$
HCN	Weaker	Stronger	CN^- wants proton $HCN \leftarrow CN^-$ $HCN + OH^- \leftarrow \Leftrightarrow CN^- + H_2O$

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
since strong acid will give up hydrogen and go to conjugate weak 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 (<u>know these</u> 6 common strong acids)

HCl (hydrochloric)
HBr (hydrobromic),
HI (hydroiodic)
H_2SO_4 (sulfuric) only first ionization strong → H+ + HSO_4^-
HNO_3 (nitric)
$HClO_4$ (perchloric)

All of above are stronger than H_3O^+ but all produce H^+ or H_3O^+ in water

Can assume other acids you encounter are weak if not one of six above.
Strong acids dissociate 100% to ionic form
(no molecules of acid remain – all ions)

Common strong bases (<u>know these</u>)
LiOH NaOH KOH $Ca(OH)_2$ $Sr(OH)_2$ $Ba(OH)_2$

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 for water

$K = \dfrac{[H^+][OH^-]}{[H_2O]}$ or $K_w = [H^+][OH^-]$

where K_w is the ionization constant for water at

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

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
$[H^+] = .020$

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

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

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

pH and pOH

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

$pH = -\log [H^+]$ or equivalent to $[H^+] = 10^{-pH}$

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

$pOH = -\log [OH^-]$ or equivalent to $[OH^-] = 10^{-pOH}$

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

$pH + pOH = 14$

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

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

<u>Example pH and pOH problems</u>
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 x10-2)
= - [log 2.0 +log 10-2]
= - [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 $[H^+]$ → $[H^+] = 10^{-pH}$ antilog (pH)

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

<u>Logarithms and significant figures:</u>

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

<u>Make sure on Calculator you are familiar with needed operations</u>

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)

<u>Indicators and Equilibrium</u>

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} = <u>$[H^+]$ $[In^-]$</u>

[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

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

HIn: green; In^-: 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 $K_a K_b = 1.0 \times 10^{-14}$

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^+	$C_2H_3O_2^-$

$HC_2H_3O_2 \Leftrightarrow H^+ + C_2H_3O_2^-$ $K_a = 1.8 \times 10^{-5}$
1.0M 1.8×10^{-5} 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 ⇔ NH_4^+ + OH^- $K_b = 1.8 \times 10^{-5}$

0.10 0.10 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 x10^{-5}

pH = 4.740

Equal amounts pH = pK_a

$HC_2H_3O_2$ ⇔ H^+ + $C_2H_3O_2^-$

1.00 1.82 x10^{-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	$HC_2H_3O_2$ ⇔	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 x10^{-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

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

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

$HC_2H_3O_2$ $\Leftrightarrow$	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

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

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.:

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

$3.50 = 3.92 + \log x$
$-0.42 = \log x$

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

$[OCN^-] = 0.38\ M$
$[HOCN] = 1.00M$

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 $[HOCN] = 1.00M$

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. NH_4^+
   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.

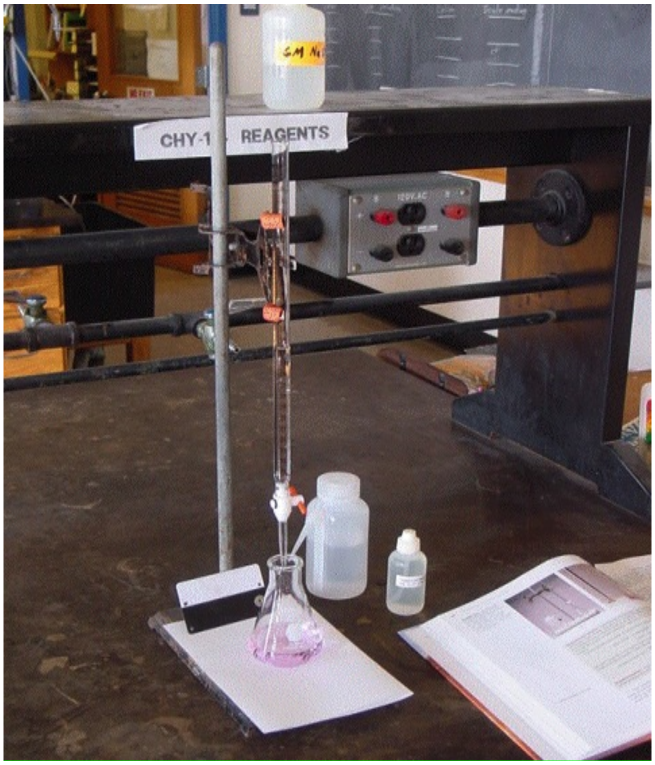
Chemical Analysis and Titrations

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



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Acid Base Titrations

1) Strong acid titrated with strong base

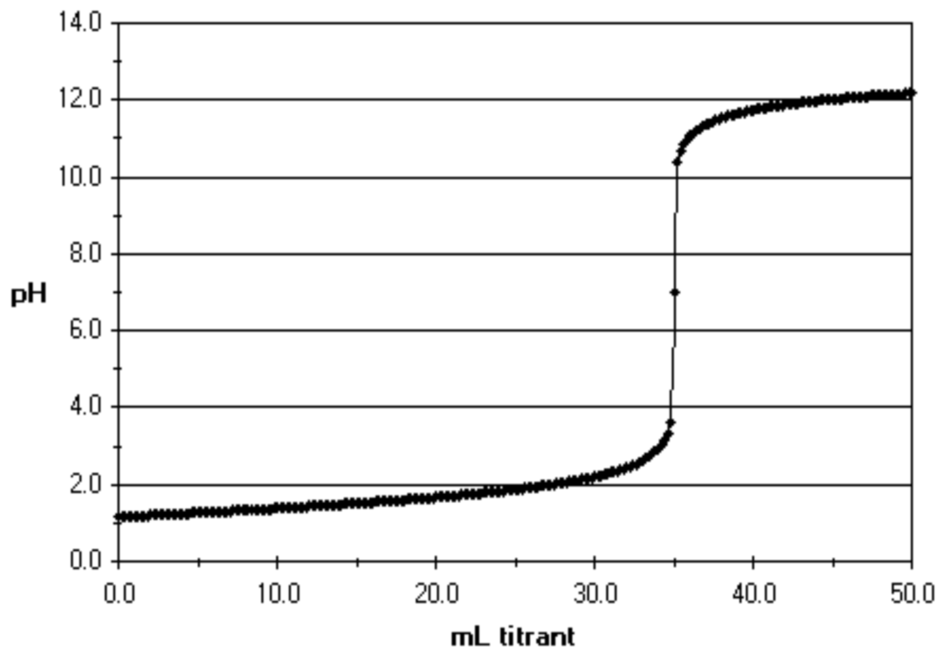
35 mL 0.1M HCl
pH = -log $[H^+]$
pH= 1.00

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

$N_AV_A = N_BV_B$ Note: N= normality

or **$n_AM_AV_A = n_BM_BV_B$**



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

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

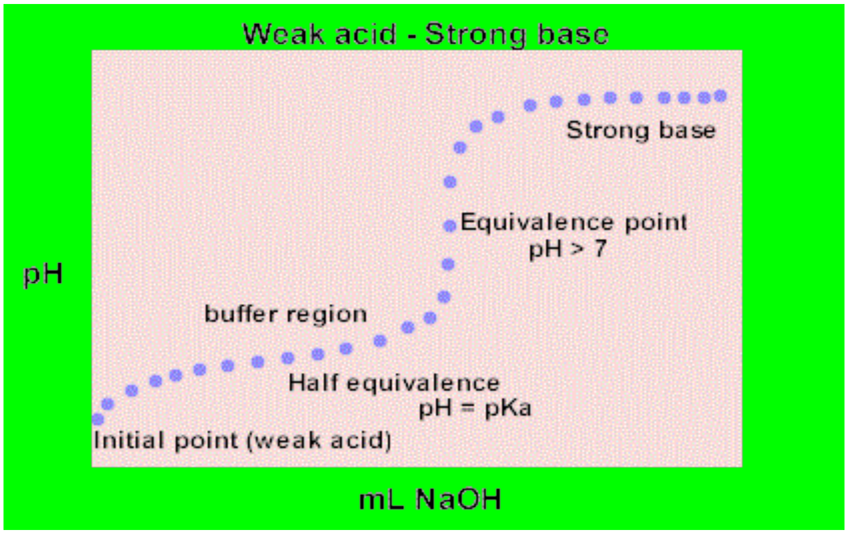
Initial pH

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

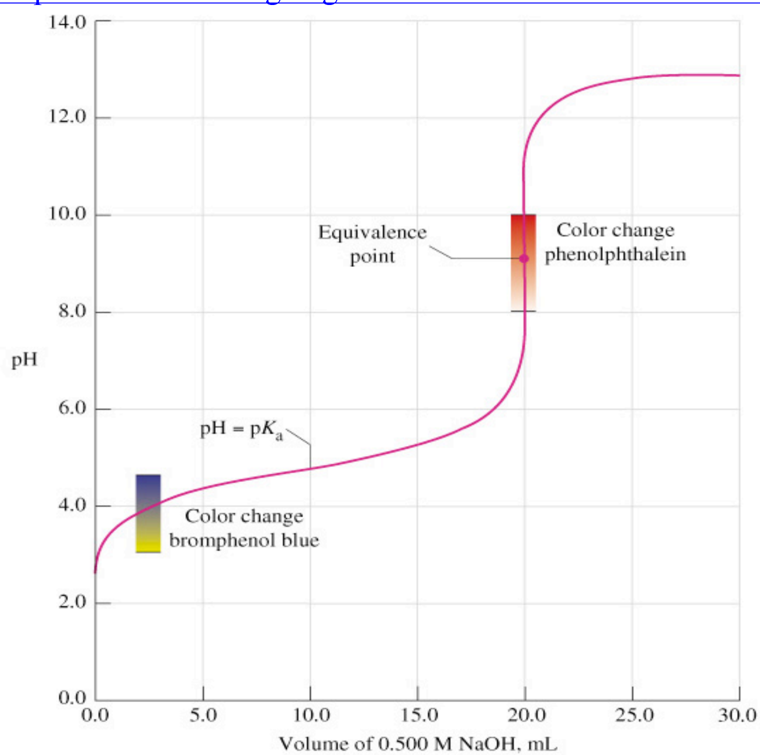
$1.8 \times 10^{-6} = x^2$

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

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% $HC_2H_3O_2$

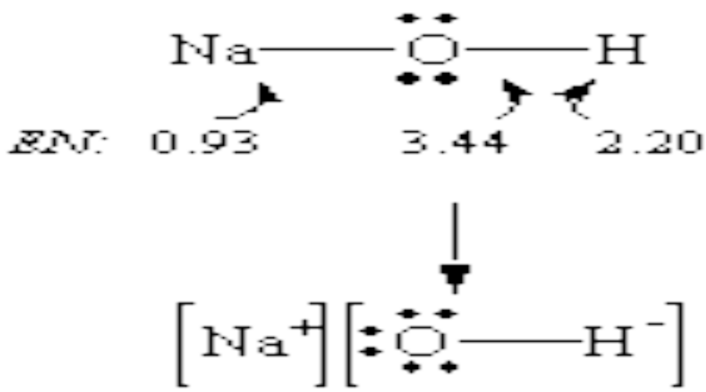
At 1/2 equivalence point:
50% $C_2H_3O_2^-$, 50% $HC_2H_3O_2$

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

Structures of Hydroxy Compounds

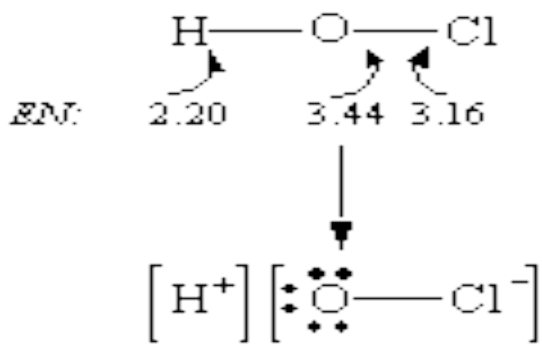
NaOH is base and HOCl is acid
Why different?

Low electronegativity tends to donate electrons to form positive species



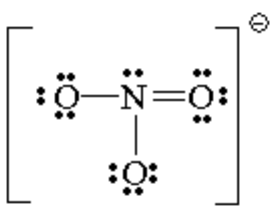
http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch11/acidbaseframe.html

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:

$$H \overset{a}{-} O \overset{b}{-} Z$$

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

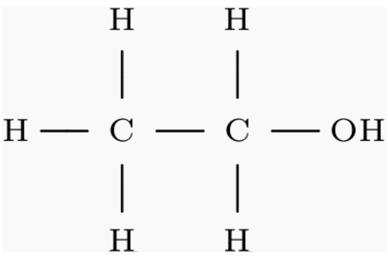
More oxygens then stronger the substance is as an acid

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 BELOW Chem 1120 can ignore

Oxidizing and Reducing Agents

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

3 most common

Oxidizing Agents reduced	Name	Color	Metal ox nu
MnO_4^-	permanganate	purple	Mn 7→ 2
CrO_4^{2-}	chromate	yellow- in base	Cr 6 → 3
$Cr_2O_7^{2-}$	dichromate	red- in acid	Cr 6 → 3

Reducing Agents

Metal is oxidized to give up electron so something else oxidizes
Metals
Mg, Zn
$Zn \rightarrow Zn^{2+} + 2e^-$ so Zn ox nu goes from 0 → 2 (oxidized)

Or metal ions (homogeneous solution)
Sn^{2+} (aq) → Sn^{4+} (aq) + $2e^-$
Sn^{4+}, metal is oxidized