ACID/BASE EQUILIBRIUM

- Several scientific theories exist that define acid-base chemistry. We will discuss THREE of these theories.

- These theories differ in the way that acids, bases, and their associated reactions are defined.

- Typically, the newer theories include MORE chemicals under the umbrella of "acid-base chemistry"!

THREE ACID-BASE THEORIES

1. Arrhenius theory
2. Bronsted-Lowry theory
3. Lewis theory

ARRHENIUS THEORY

- The oldest model of acid-base chemistry!

- Only applicable to systems where WATER is the solvent!

ACIDS are substances that ionize in water to increase the concentration of HYDRONIUM ION

Hydronium ion

or, for simplicity:

"Hydrogen ion" - doesn't really exist as a free ion in water, but a convenient simplification!

ARRHENIUS THEORY

BASES are substances that ionize in water to increase the concentration of HYDROXIDE ION

For soluble metal hydroxides:

$$MOH \xrightleftharpoons{H_2O} M^+ + OH^-$$

$$NaOH \rightarrow Na^+ + OH^-$$

Hydroxide ion

For other Arrhenius bases:

$$B + H_2O \rightleftharpoons BH^+ + OH^- \quad \text{ex: } NH_3$$

An Arrhenius acid base reaction can be represented by:

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O$$

"neutralization"

or, using hydrogen ion instead of hydronium

$$H^+ + OH^- \rightleftharpoons H_2O$$

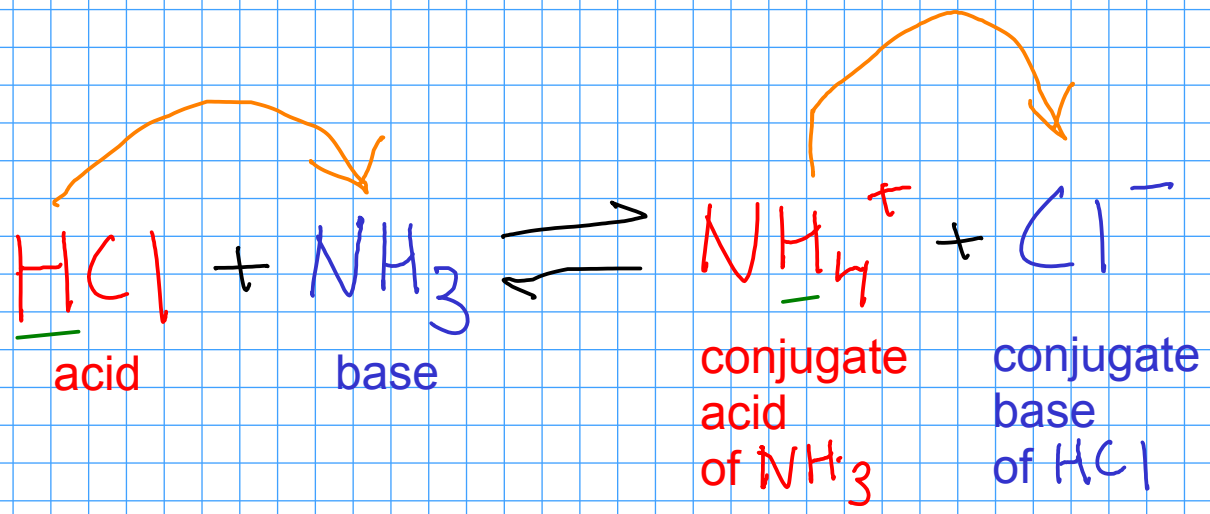
BRONSTED-LOWRY THEORY

H^+ ions!

- Bronsted-Lowry theory views acid-base reactions as PROTON TRANSFER reactions!

ACIDS are PROTON DONORS

BASES are PROTON ACCEPTORS



A CONJUGATE PAIR is an acid and a base that differ by a proton!

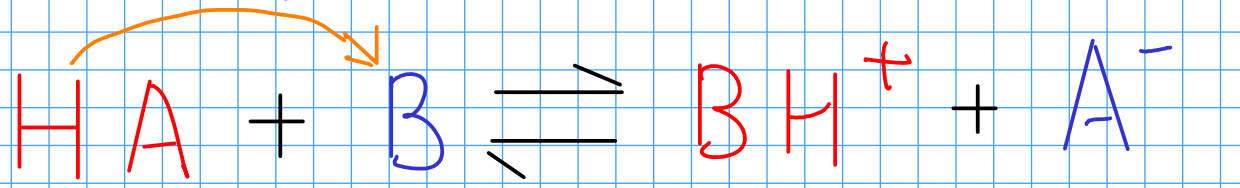
... a few examples of conjugate pairs:

RED for acid

BLUE for base

Species	Conjugate
NH_3	NH_4^+
H_2O	OH^-
H_2O	H_3O^+
$HC_2H_3O_2$	$C_2H_3O_2^-$

A generic Bronsted-Lowrey acid.base reaction:



acid

base

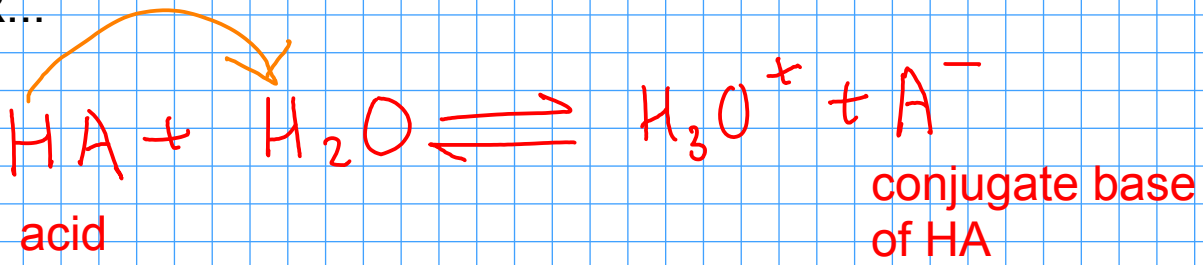
conjugate acid of B

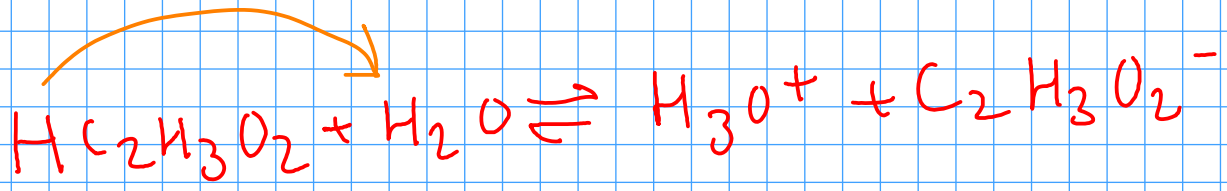
conjugate base of HA

... you should be able to write the products of a Bornsted-Lowry acid-base reaction, identifying the CONJUGATE PAIRS

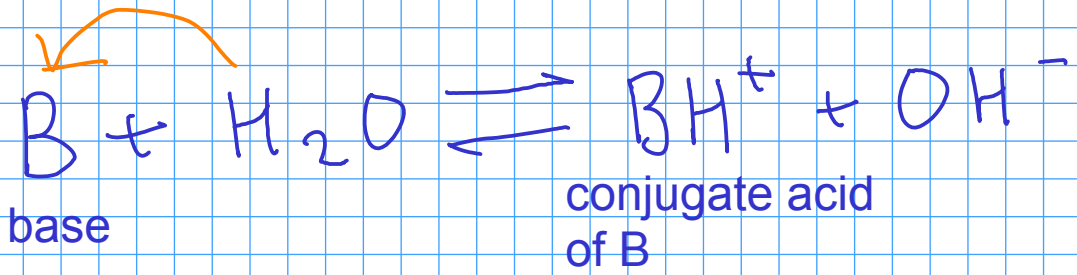
BRONSTED-LOWRY THEORY

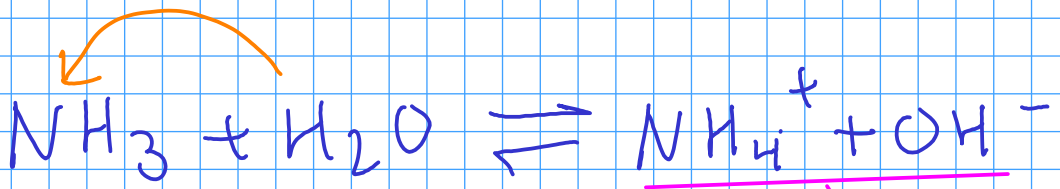
IN WATER...





Acetic acid and water





Ammonia and water

This is why we often call an ammonia/water solution "ammonium hydroxide"!

In the red reactions, water functions as a base. In the blue reactions, water functions as a acid!

LEWIS THEORY

- Lewis theory treats acid-base chemistry as ELECTRON-TRANSFER chemistry involving pairs of electrons

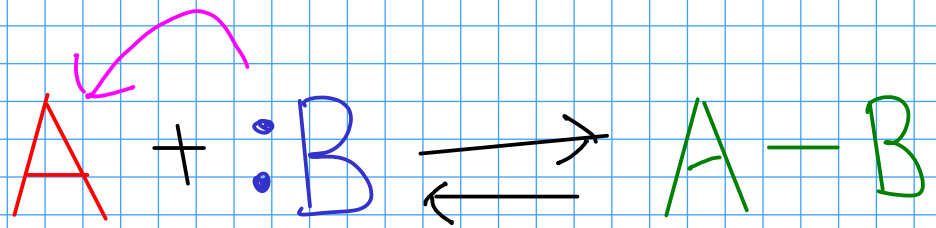
- Lewis acid-base reactions form new covalent bonds (of interest to organic chemists!)

ACIDS are ACCEPTORS of electron pairs

... this is why some METAL IONS, even though they contain no hydorgen ions, can exhibit ACIDIC character. Many metal ions can accept a pair of electrons to form a COMPLEX with a Lewis base!

BASES are DONORS of electron pairs.

... so, Lewis bases have LONE PAIRS OF ELECTRONS in their Lewis structures



Lewis acid

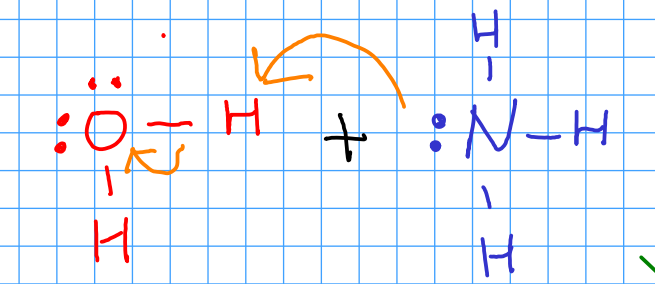
Lewis base

... In a Lewis acid-base reaction, electrons are doneted from the Lewis base to the Lewis acid. This forms a new COVALENT BOND between the acid and the base.

LEWIS THEORY

Example: ammonia and water

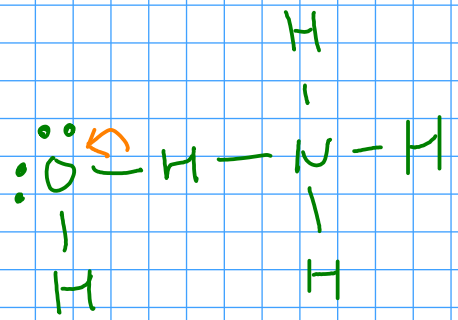
$$H_2O + :NH_3 \rightleftharpoons NH_4^+ + OH^-$$

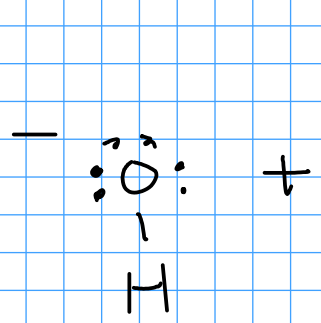


water
(Lewis acid)

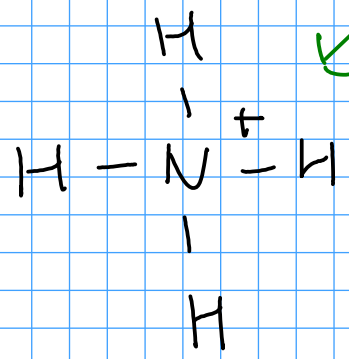
ammonia
(Lewis base)

Ammonia donates
a pair of electrons to
a hydrogen on the water molecule,
forming a new covalent bond (and breaking another)





hydroxide ion



ammonium ion

Overall: $H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$

COMPARING THE THEORIES

- From Arrhenius to Lewis, the definitions get broader as you go along. In other woeds, the later definitions include MORE SUBSTANCES under the acid/base umbrella.

If something is an Arrhenius acid, it is also an acid in the Bronsted or Lewis picture.

If something is an Arrhenius base, it is also a base in the Bronsted or Lewis picture.

All Bronsted acids are Lewis acids, and all Bronsted bases are Lewis bases.

... but not all Lewis acids/bases (like the metal ions) are Bronsted or Arrhenius acids/bases.

... We will primarily use the BRONSTED-LOWRY theory from this point in the course!

WATER CHEMISTRY

- Water self-ionizes!

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

or

$$H_2O \rightleftharpoons H^+ + OH^-$$

This is an equilibrium reaction!

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

[X] = molar concentration of "X"

In aqueous solution, $[H_2O]$ is essentially constant, so we roll that into K.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

WATER CHEMISTRY

- The self-ionization of water has a small equilibrium constant. What does this imply?

THE CONCNETRATION OF HYDROXIDE AND HYDRONIUM ION IN PURE WATER IS VERY SMALL!

How small?

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

In pure water, the concentration of hydroxide and hydronium must be equal, since they are formed at the same time and at the same ratio from the ionization reaction of water.

$$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$$

Let "z" = $[H_3O^+] = [OH^-]$

$$z^2 = 1 \times 10^{-14}$$

$$z = 1 \times 10^{-7}\ \underline{M}$$

"p" NOTATION

- "p" notation helps us deal with the very small numbers we encounter when working with acids, bases, and water.

- based on log base 10

"p" means $-\log_{10}$

log ~~ln~~

So,

$$pH = -\log_{10}[H_3O^+] \qquad [H_3O^+] = 10^{-pH}$$

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

"p" NOTATION

- Apply "p" notation to the water self-ionization reaction!

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$$

becomes ...

$$pK_w = pH + pOH = 14.00$$

Taking the "p" (negative log base ten) of the equilibrium constant is often used for BUFFER SOLUTIONS, which we'll discuss later!

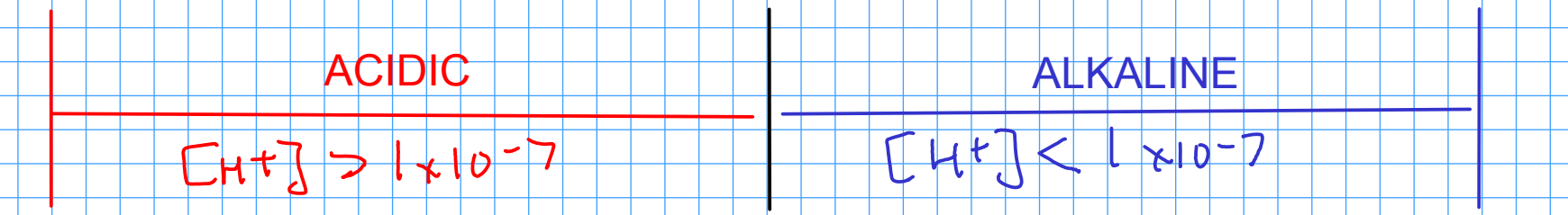
ACIDITY AND ALKALINITY

- At pH = 7, pH = pOH. The solution is considered NEUTRAL
  - Also, $[H^+] = [OH^-]$!

- At pH <7, pH < pOH. The solution is considered ACIDIC
  - Also, $[H^+] > [OH^-]$!

- At pH > 7, pH > pOH. The solution is considered ALKALINE (BASIC)
  - Also, $[H^+] < [OH^-]$!

The pH scale...



pH AND TEMPERATURE

$$pK_w = pH + pOH = 14.00$$

This equation is valid at room temperature, specifically 25 °C.

Equilibrium constants depend on TEMPERATURE, and change with temperature.

So, the "neutral" pH (where the concentration of hydroxide and hydronium ions are equal) CHANGES with changing temperatures

This change is important at temperatures greatly different from 25 °C.

As an example, consider average "normal" human body temperature: 37° C

At 37°C, $pK_w = 13.60$

pH of neutral solution = 6.8

ACID-BASE EQUILIBRIUM IN WATER

- Like other ELECTROLYTES, acids and bases IONIZE to some extent in water

- STRONG electrolytes ionize completely. Acids and bases that ionize completely in water are called STRONG ACIDS and STRONG BASES

- WEAK electrolytes ionize partially, remaining mostly non-ionized. Acids and bases that ionize only partially in solution are called WEAK ACIDS and WEAK BASES.

- Most acids and bases are WEAK!

Common strong acids

HCl

HNO_3

H_2SO_4 (only 1st proton)

HBr

HI

Common strong bases

$NaOH$] alkali metal hydroxides

KOH]

$Ca(OH)_2$

SIMPLE pH CALCULATIONS: STRONG ELECTROLYTES

- With strong acids and bases, the acid or base completely ionizes in water. So, we only have to worry about the effect of the acid or base on the water equilibrium itself.

- Since the equilibrium constant for the self-ionization of water is so small, the strong acid or base will overpower the hydronium (for acids) or hydroxide (for bases) produced by the water.

$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$

Consider 0.025 M HNO_3

Assume all H_3O^+ comes from acid!

$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

So, $[H_3O^+] = 0.025\ M$

$pH = 1.60$

significant digits are after decimal!

$pOH = 14.00 - pH$

$pOH = 12.40$

Usually, we are interested in calculating pH and don't really care what pOH is!

Consider 0.0125 M NaOH

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

Assume all OH^- comes from base

$NaOH \rightarrow Na^+ + OH^-$

$[OH^-] = 0.0125\ M$

$pOH = 1.90$

In a solution of strong base, the only source of hydronium ion is the water equilibrium!

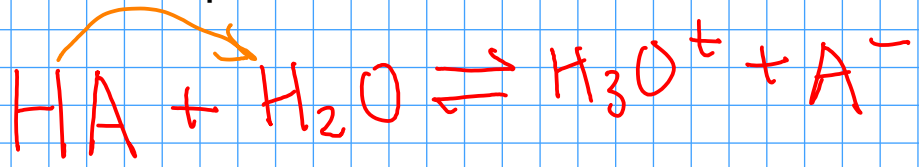
$pH = 14.00 - pOH$ ← $2H_2O \rightleftharpoons H_3O^+ + OH^-$

$pH = 12.10$

$[H^+] = 1 \times 10^{-12.10} = 7.9 \times 10^{-13}\ M$

This is the concentration of hydronium ion produced by the water equilibrium. It's also equal to the concentration of HYDROXIDE ion produced by the water. As you can see, it's MUCH, MUCH smaller than the 0.0125 M produced by the base!

For a WEAK ACID, equilibrium does not lie far to the right. The ionization equilibrium of the acid itself is important!



$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Again, water's concentration will not change significantly, so it is folded into the ionization constant

K_a: acid ionization constant

[HA] = concentration of undissociated acid

For a WEAK BASE, equilibrium does not lie far to the right. The ionization equilibrium of the base itself is important!

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

K_b: base ionization constant

WEAK ELECTROLYTES

- In solutions of weak acids or bases, the UNDISSOCIATED form is present in significantly high concentration.

- The pH of a solution of weak acid will be HIGHER than the pH of a strong acid solution with the same nominal concentration!

- The pH of a solution of weak base will be LOWER than the pH of a strong base solution with the same nominal concentration!

Consider a 0.100M solution of the WEAK ACID HNO_2

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$$

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = 5.1 \times 10^{-4}$$

values for Ka are determined experimentally

What is the pH of the solution?

To find the pH, we need to determine the concnetration of hydronium $[H_3O^+]$

... so we need to solve the equilibrium expression. But we don't know all of the concentrations AT EQUILIBRIUM to do so!

... but they ARE related!

We assume the amount of hydronium from the water is small enough to ignore

SPECIES	INITIAL CONC	CHANGE	EQUILIBRIUM CONC
$[H_3O^+]$	0	$+x$	x
$[NO_2^-]$	0	$+x$	x
$[HNO_2]$	0.100	$-x$	$0.100 - x$

... this is similar to the problems from the equilibrium chapter!

$$5.1 \times 10^{-4} = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

$$5.1 \times 10^{-4} = \frac{(x)(x)}{(0.100 - x)}$$

$$5.1 \times 10^{-4} = \frac{x^2}{0.100 - x}$$

Quadratic equation!

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

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Assume that x << 0.100

$$5.1 \times 10^{-4} = \frac{x^2}{0.100}$$

$$x^2 = 5.1 \times 10^{-5}$$

$$x = 7.14 \times 10^{-3} = [H_3O^+]$$

$$pH = \boxed{2.15}$$

What's this?
For situations where the amount of dissociated acid or base is much, much smaller than the original amount, it's safe to assume that the amount of undissociated acid remains relatively constant.

In this case, 0.100 - x is essentially the same thing as 0.100 .

... if we'd used the quadratic equation, our answer would have been pH = 2.16

Compare:

- Weak acid HNO_2 : pH of 0.10 M solution = 2.15

- Strong acid: pH of 0.10 M solution = 1.00

The stronger the acid, the lower the pH of a solution of given concentration will be!

Consider an 0.100 M solution of the weak base ammonia:

NH_3 ; $K_b = 1.75 \times 10^{-5}$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = 1.75 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

What is the pH?

	initial	Δ	equilibrium
$[NH_4^+]$	0	$+x$	x
$[OH^-]$	0	$+x$	x
$[NH_3]$	.100	$-x$	$.100 - x$

Plugging into the equilibrium expression, we get:

$$1.75 \times 10^{-5} = \frac{x^2}{.100 - x}$$

Solve for "x"!

$$1.75 \times 10^{-5} = \frac{x^2}{.160 - x}$$

Quadratic!

$x \ll 0.100$ Assume $.100 - x \approx .100$

$$1.75 \times 10^{-5} = \frac{x^2}{.100}$$

$1.322 \times 10^{-3} = x = [OH^-]$

$-\log(x) = pOH$

$2.88 = pOH$

$pH + pOH = 14.00$

$\boxed{pH = 11.12}$

Remember that the -log(x) is NOT equal to the pH this time.

Since we defined x as the HYDROXIDE concentration, the -log(x) = pOH !

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

... solving by the quadratic equation gives an answer of pH = 11.12

Compare pH to the pH of an 0.100 M solution of the strong base NaOH:

$pH_{,NH_3} = 11.12$

$NaOH \longrightarrow Na^+ + OH^-$

$[OH^-] = 0.100$

$pOH = 1.00$

$pH + pOH = 14.00$

$\boxed{pH = 13.00}$

The higher the Ka or Kb value, the stronger the acid or base!