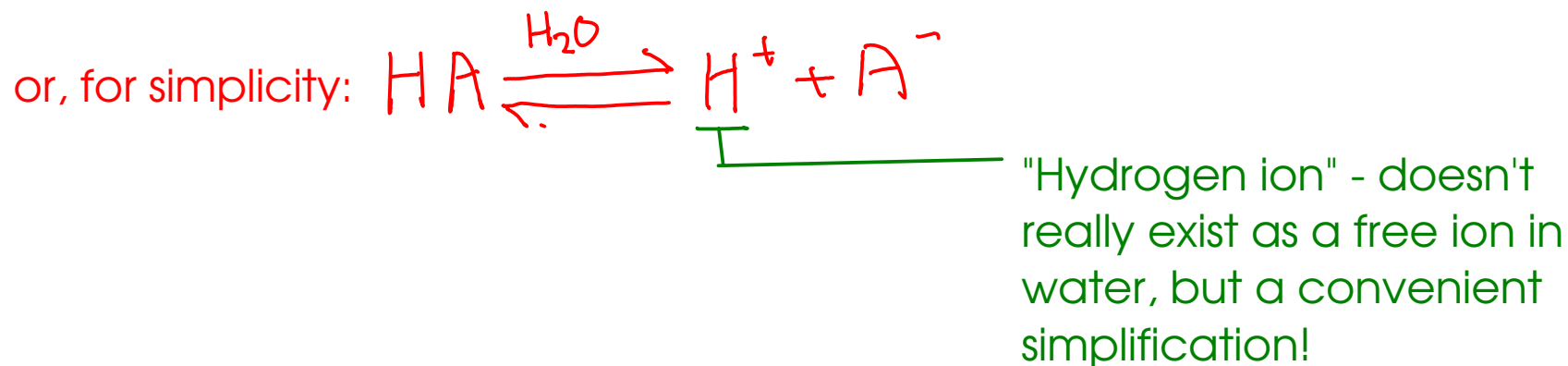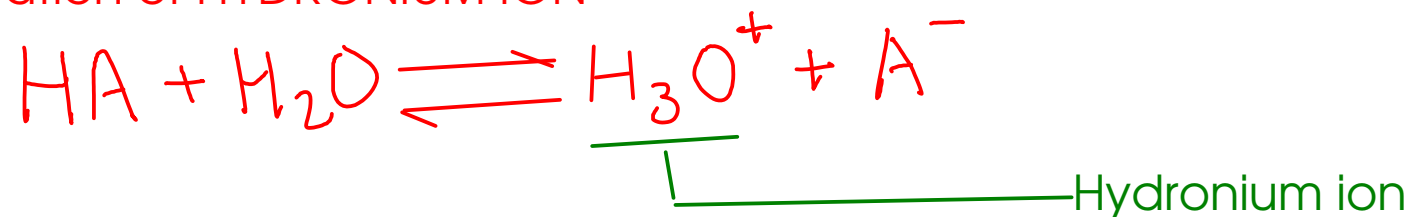# ARRHENIUS THEORY

- 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

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

————Hydronium ion

or, for simplicity:
$$HA \underset{}{\overset{H_2O}{\rightleftharpoons}} H^+ + A^-$$

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

ARRHENIUS THEORY

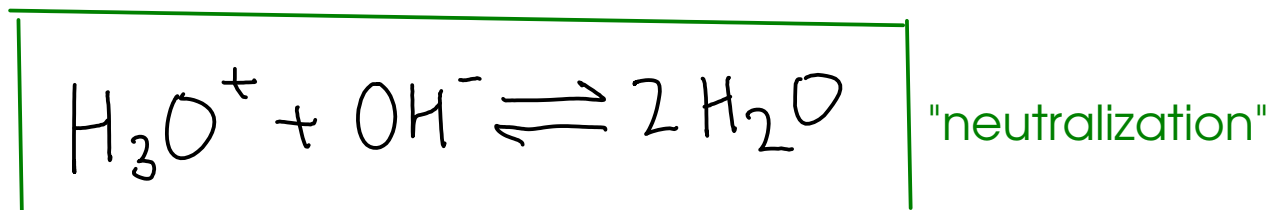BASES are substances that ionize in water to increase the concentration of HYDROXIDE ION

For soluble metal hydroxides:

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

$$MOH \underset{\longleftarrow}{\overset{H_2O}{\rightleftharpoons}} M^+ + OH^-$$

— Hydroxide ion
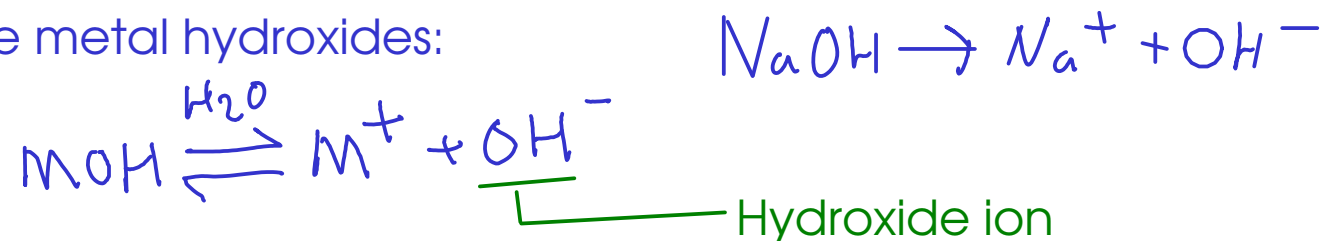
For other Arrhenius bases:

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

An Arrhenius acid base reaction can be represented by:

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

"neutralization"

or, using hydrogen ion instead of hydronium

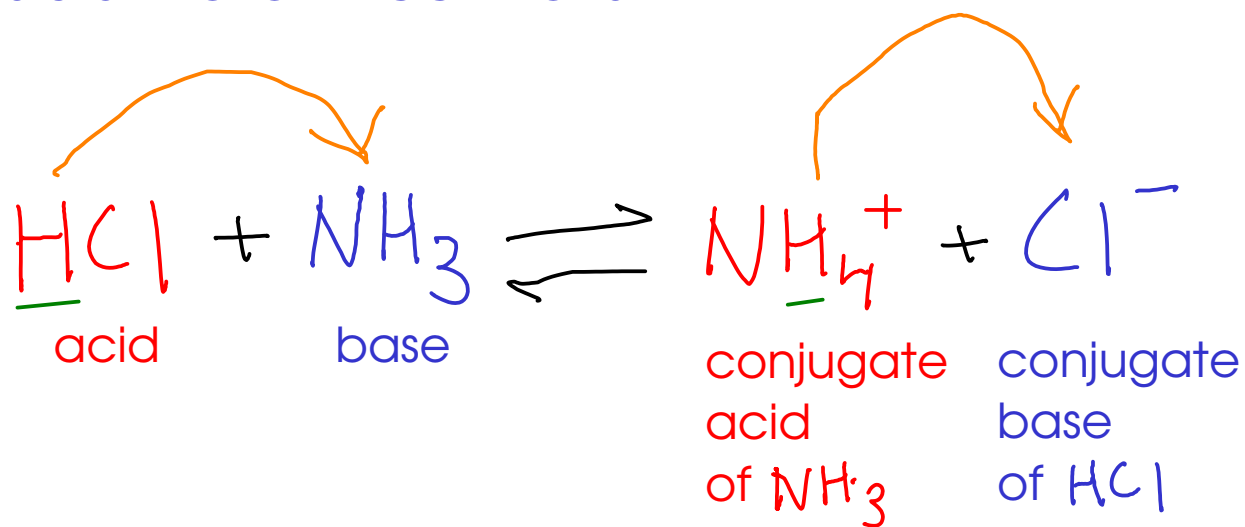$$H^+ + OH^- \rightleftharpoons H_2O$$

BRONSTED-LOWRY THEORY

$-H^+$ ions !

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

ACIDS are PROTON DONORS

BASES are PROTON ACCEPTORS

$$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$

acid   base   conjugate   conjugate
                acid   base
                of NH_3 of HCl

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:

$$HA + B \rightleftharpoons BH^+ + A^-$$

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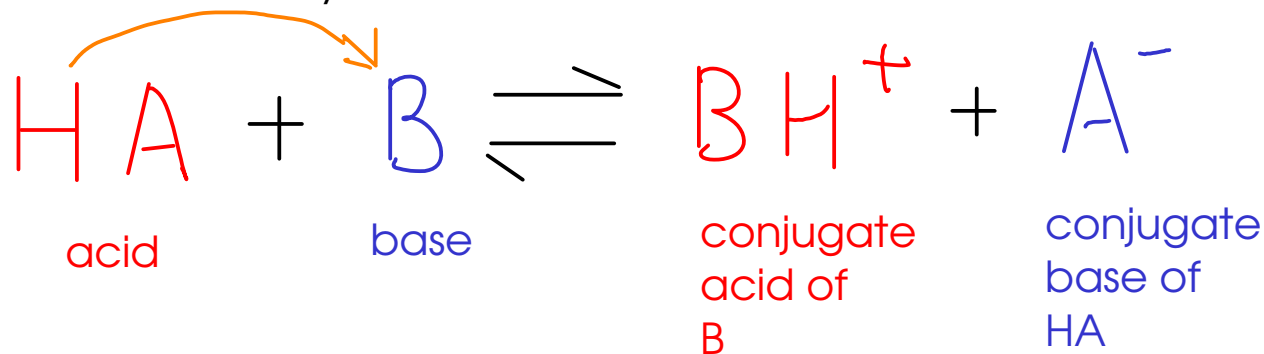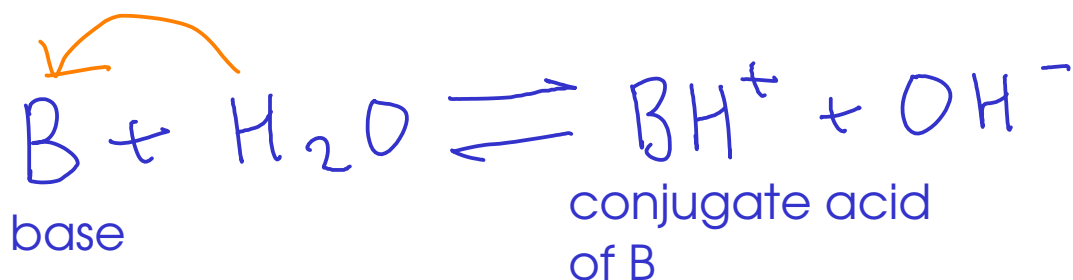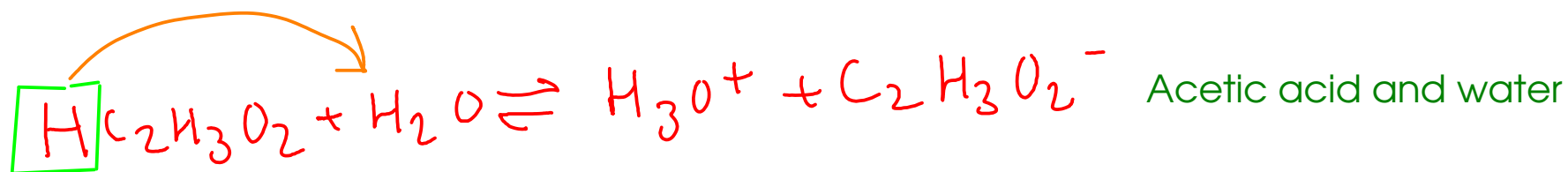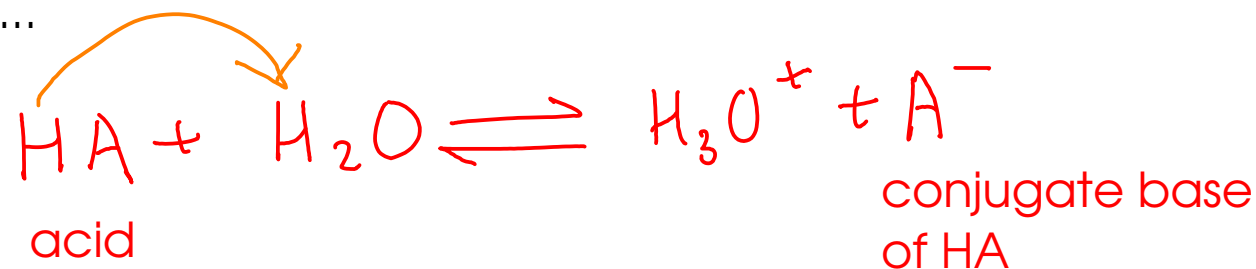
... you should be able to write the products of a Bronsted-Lowry acid-base reaction, identifying the CONJUGATE PAIRS

BRONSTED-LOWRY THEORY

IN WATER...

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

acid   conjugate base
                        of HA

$$\boxed{H}C_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$ Acetic acid and water

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

base   conjugate acid
                        of B

$$NH_3 + \boxed{H_2O} \rightleftharpoons NH_4^+ + OH^-$$ Ammonia and water
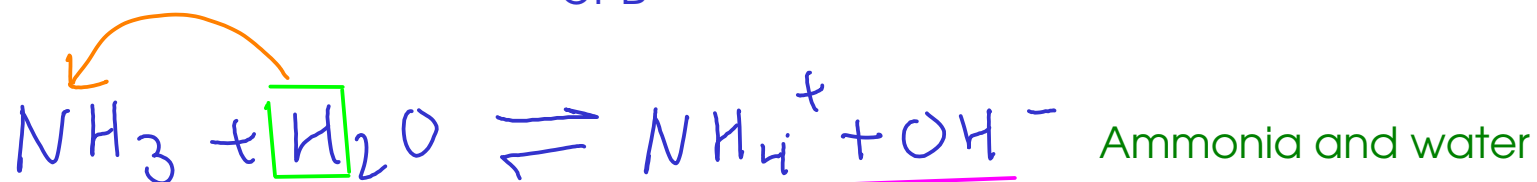
This is why we often call an ammonia/water
solution "ammonium hydroxide"!

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! ex: $Ag(NH_3)_2^+$
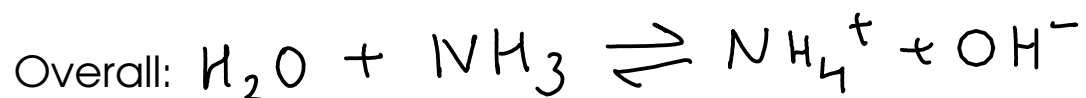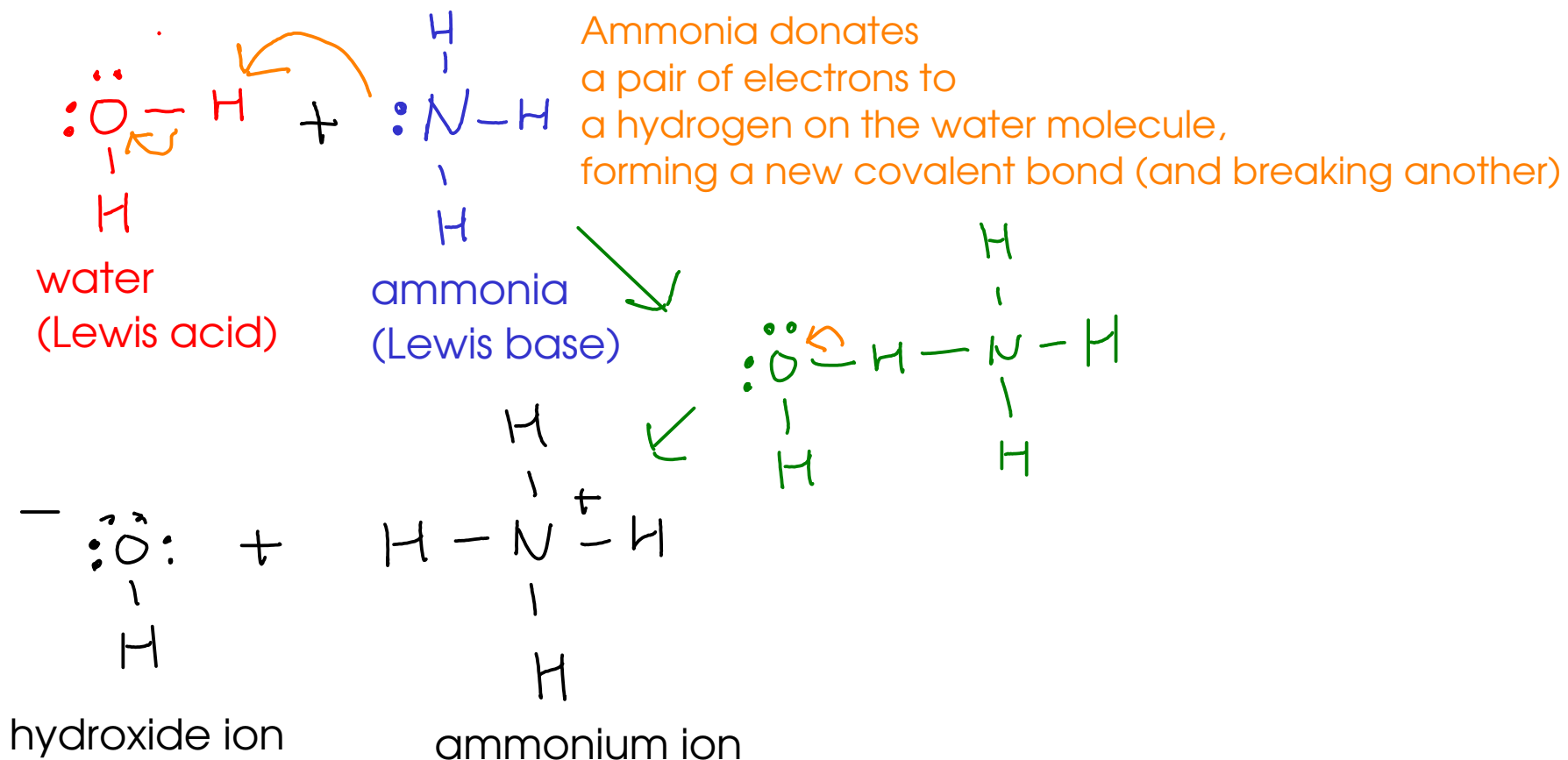
BASES are DONORS of electron pairs.

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

$$A + :B \rightleftharpoons A-B$$

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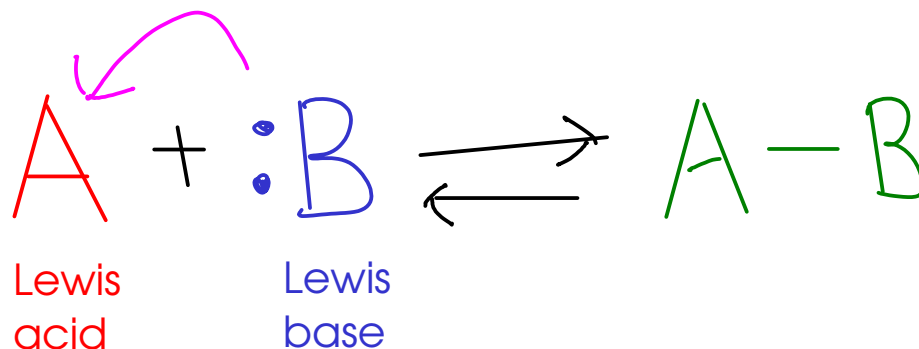
... In a Lewis acid-base reaction, electrons are donated from the Lewis base to the Lewis acid. This forms a new COVALENT BOND between the acid and the base.

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: $H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$
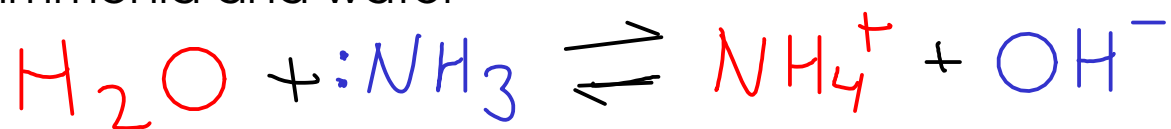
COMPARING THE THEORIES

- 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.
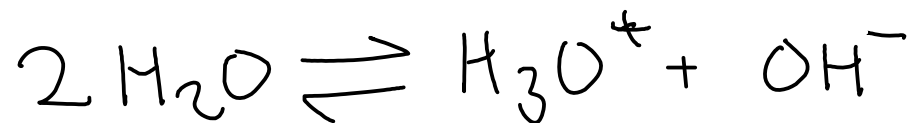
ARRHENIUS

BRONSTED-LOWRY

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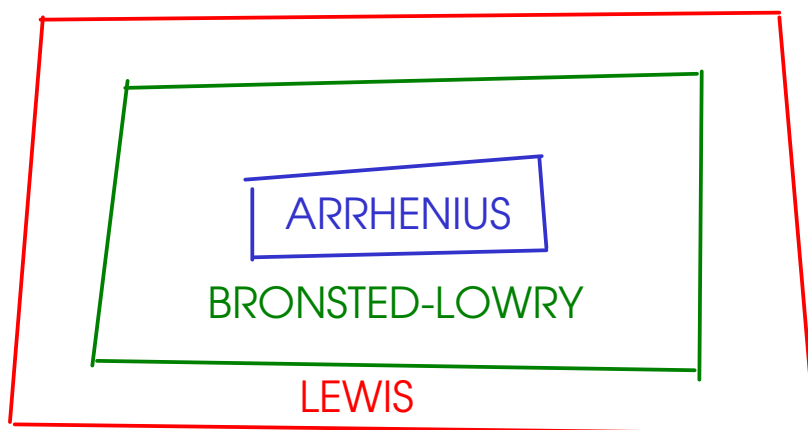
... We will primarily use the BRONSTED-LOWRY theory from this point in the course!

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"

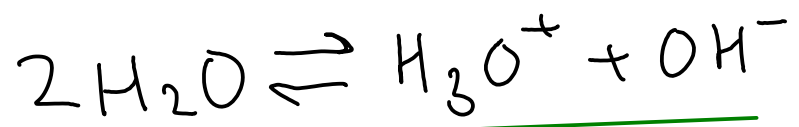In aqueous solution, (H_2O) is essentially constant, so we roll that into K.

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

WATER CHEMISTRY

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

THE CONCENTRATION 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.

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

Solve... Let $x = [H_3O^+] = [OH^-]$

$$(x)(x) = 1.0 \times 10^{-14}$$

$$x^2 = 1.0 \times 10^{-14}$$

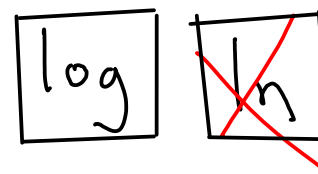$$x = 1.0 \times 10^{-7} M = [H_3O^+] = [OH^-]$$

"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

On a calculator, use

$$\boxed{\log} \quad \boxed{\cancel{\ln}}$$

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

So,

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

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

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

$$[OH^-] = 10^{-pOH}$$

"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...

ACIDIC

$[H^+] > 1 \times 10^{-7}$

ALKALINE

$[H^+] < 1 \times 10^{-7}$

pH = 0

pH = 7
NEUTRAL

$[H^+] = 1 \times 10^{-7}$

pH = 14
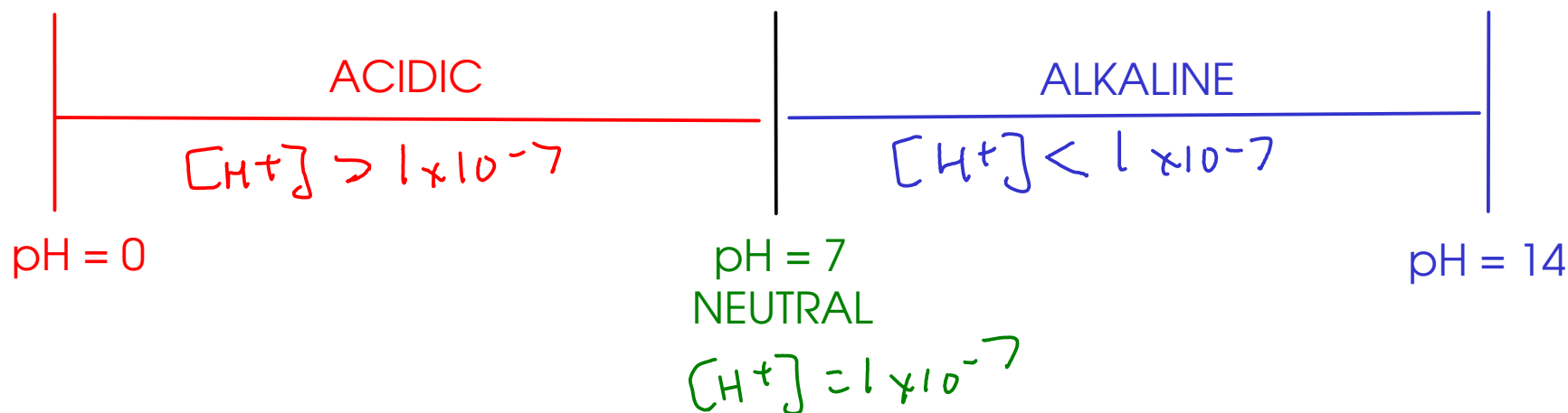
pH AND TEMPERATURE

$$pK_w = pH + pOH = 14.00$$

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
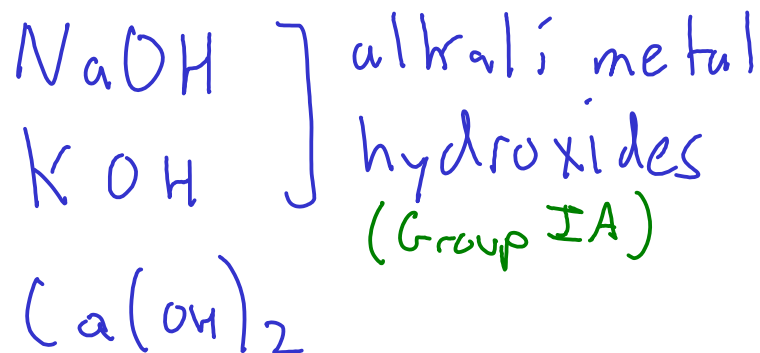
At 37°C, $pK_w = 13.60$

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
KOH] hydroxides
(Group IA)

$Ca(OH)_2$

SIMPLE pH CALCULATIONS: STRONG ELECTROLYTES

- With strong acids and bases, the acid or base <u>completely ionizes</u> 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.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \; ; \; K_w = 1.0 \times 10^{-14}$$
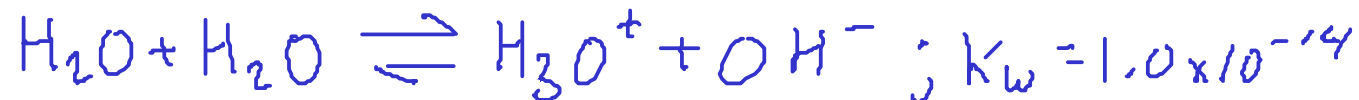
Consider a solution of 0.025 M nitric acid (a strong acid):

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$$
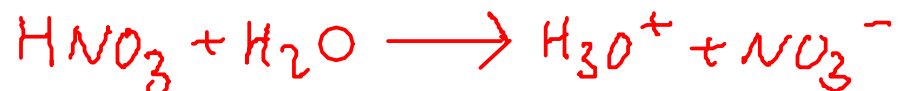
Assume that all of the hydronium ion present at equilibrium comes from the acid (contribution of the water equilibrium itself is minimal)

$$So, [H_3O^+] = nominal \; [HNO_3] = 0.025 \; M \; H_3O^+$$

$$pH = -\log_{10}(0.025) = \boxed{1.60}$$

For logarithms, the places AFTER the decimal point are significant digits, while the numbers in front of the decimal point are not (they're the exponent in the original number.)

What would the hydroxide ion concentration be?

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

$$(0.025)[OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = 4.0 \times 10^{-13} \; \underline{M}$$

... this equals the amount of water that dissociates!

Consider a solution of 0.0125 M sodium hydroxide (a strong base):

Again, let's assume that the base provides all of the hydroxide in solution

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

$$[OH^-] = nominal\ [NaOH] = 0.0125\ \underline{M}\ OH^-$$

$$pOH = -\log_{10}(0.0125) = 1.90$$

... now change pOH to pH so we can compare this to the acid problem we just solved:

$$pH + pOH = 14.00$$

$$pH + 1.90 = 14.00$$

$$\boxed{pH = 12.10}$$

Let's find the concentration of the hydronium ion, since that concetration equals the amount of water that ionized (and the amount of hydroxide produced by the water equilibrium). We assumed that this number was much less than 0.0125

$$[H_3O^+] = 10^{-12.10}$$

$$= 7.9 \times 10^{-13}\ \underline{M}$$

... which is indeed much less than 0.0125