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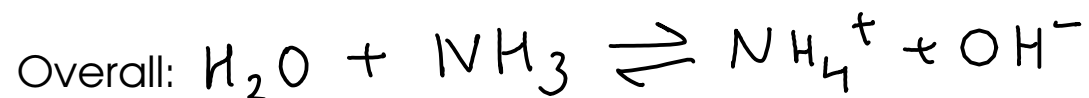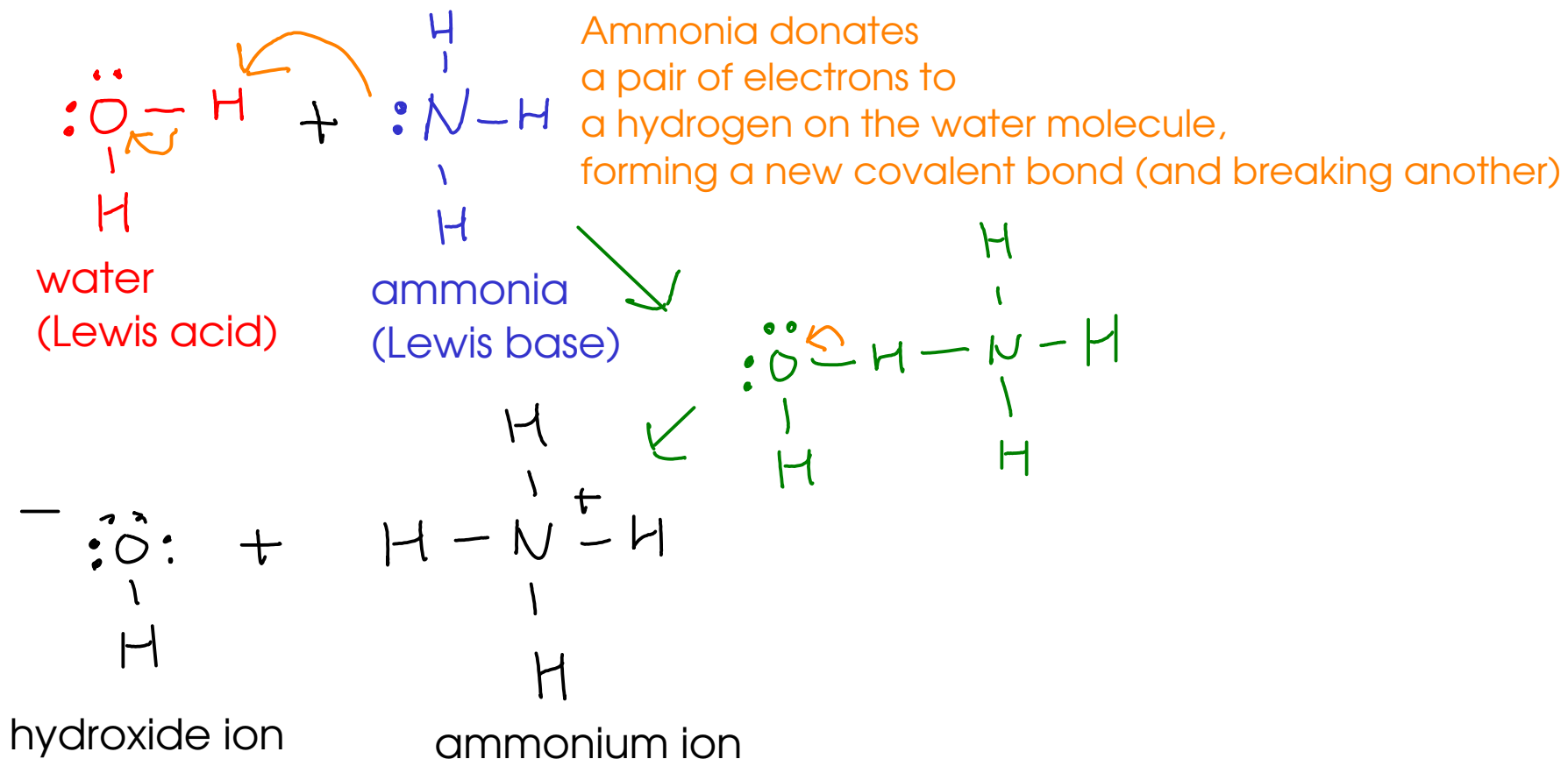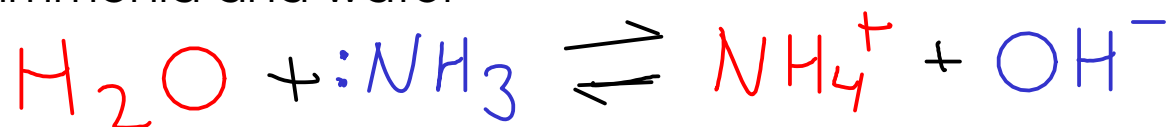
COMPARING THE THEORIES

- 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.

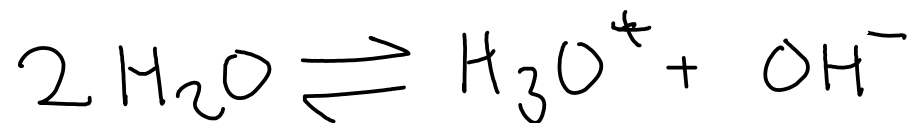All Bronsted acids are Lewis acids, and all Bronsted bases are Lewis bases.

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

ARRHENIUS

BRONSTED-LOWRY

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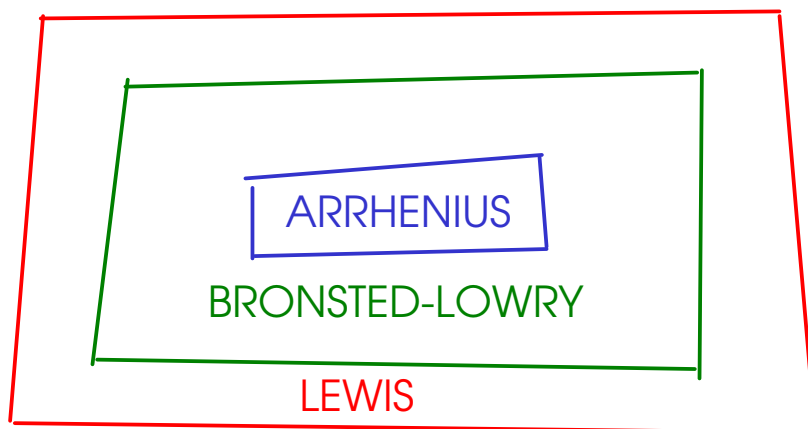
... We will primarily use the BRONSTED-LOWRY theory from this point in the course!

WATER CHEMISTRY

- Water self-ionizes!

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

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.

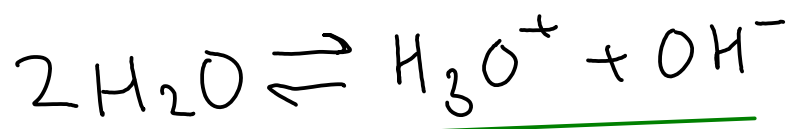$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

This is the value at 25C

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 $'x' = [H_3O^+] = [OH^-]$

$$(x)(x) = 1 \times 10^{-14}$$

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

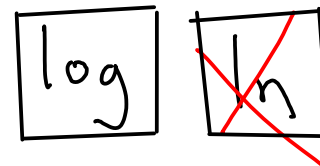$$x = 1 \times 10^{-7} M = [H_3O^+] = [OH^-]$$

"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

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

"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

$$\text{Also, } [H^+] = [OH^-]!$$

- At pH < 7, pH < pOH. The solution is considered ACIDIC

$$\text{Also, } [H^+] > [OH^-]!$$

- At pH > 7, pH > pOH. The solution is considered ALKALINE (BASIC)

$$\text{Also, } [H^+] < [OH^-]!$$

The pH scale...

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

pH = 0   pH = 7   pH = 14
                          NEUTRAL
                          $[H^+] = 1 \times 10^{-7}$
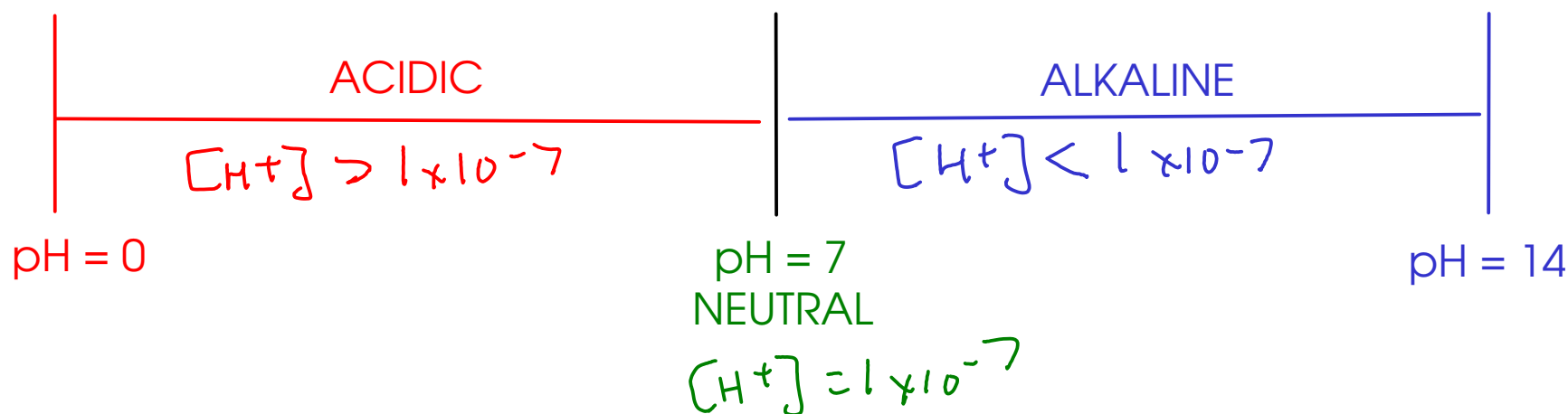
pH AND TEMPERATURE

$$pK_w = pH + pOH = 14.00$$

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, $pK_w = 13.60$
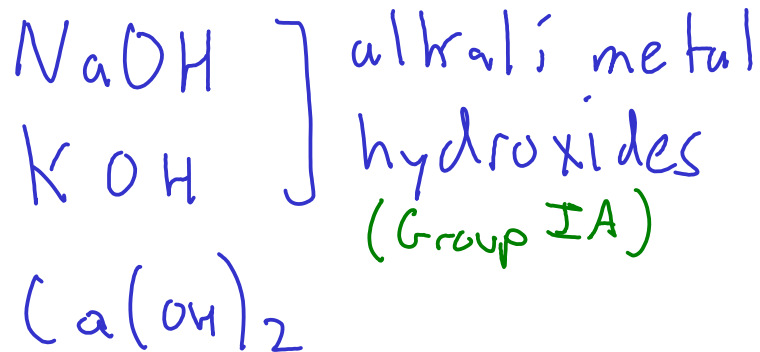
pH of neutral solution = 6.8

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 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.

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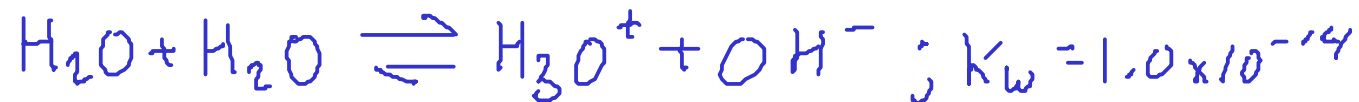
Consider a solution of 0.025 M nitric acid (a strong acid):

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

Assume all of the hydronium ion in solution comes from the acid, since the acid suppresses the self-ionization of water (Le Chateleir's principle!)

$$So, \; [H_3O^+] = [HNO_3]_{nominal} = 0.025 \; \underline{M} \; H_3O^+$$

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

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

What would the hydroxide ion concentration be under these conditions?

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

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

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

... this equals the amount of water that has self-ionized

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

$$NaOH(aq) \longrightarrow Na^+(aq) + OH^-(aq)$$

Like before, we will assume that all the hydroxide ion in solution comes from the sodium hydroxide.

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

We'd like to know pH. First, find pOH:

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

... and pOH is related to pH.

$$pH + pOH = 14.00$$

$$pH + 1.90 = 14.00$$

$$\boxed{pH = 12.10}$$

Let's find out the hydronium ion concentration here, since that will indicate how much water has self-ionized. (We assumed that the amount of water that had self-ionized was insignificant)

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

$$[H_3O^+] = 7.9 \times 10^{-13} \ \underline{M} \ H_3O^+$$

... which is MUCH SMALLER than 0.0125 ...

(A) What is the concentration of hydronium ion in an aqueous solution whose pH is 10.50? (B) What is the hydroxide ion concentration? (C) What molar concentration of sodium hydroxide solution would provide this pH?

A) $pH = 10.50$, $[H_3O^+] = ?$

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

$$[H_3O^+] = 10^{-10.50} = \boxed{3.2 \times 10^{-11} \text{ M } H_3O^+}$$

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

$$(3.2 \times 10^{-11})[OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = \boxed{3.2 \times 10^{-4} \text{ M } OH^-}$$

C) $NaOH \rightarrow Na^+ + OH^-$ — Sodium hydroxide is a STRONG BASE and should completely ionize.

1:1 ratio of $NaOH : OH^-$
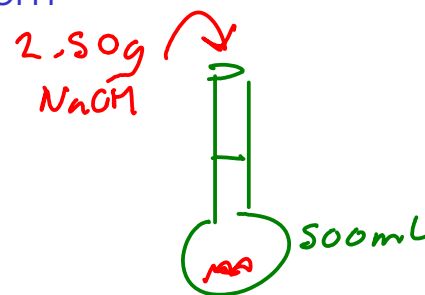
$$\boxed{[NaOH]_{numerical} = 3.2 \times 10^{-4} \text{ M}}$$

What is the pH of a sodium hydroxide solution made from dissolving 2.50 g of sodium hydroxide in enough water to make 500.0 mL of solution?

NaOH: 40.00 g/mol

2.50g NaOH

Find the molarity of the NaOH solution

$$M = \frac{mol\ NaOH}{L\ solution}$$

0.5000 L

500 mL

$$2.50\ g\ NaOH \times \frac{mol\ NaOH}{40.00\ g\ NaOH} = 0.0625\ mol\ NaOH$$

$$M = \frac{mol\ NaOH}{L\ solution} = \frac{0.0625\ mol\ NaOH}{0.5000\ L} = 0.125\ M\ NaOH$$

Sodium hydroxide is a STRONG BASE, so we expect it to ionize completely in solution and control the amount of hydroxide present.

$$NaOH \rightarrow Na^+ + OH^-\ ;\ [OH^-] = [NaOH]_{nominal} = 0.125\ \underline{M}\ OH^-$$

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

$$[H_3O^+](0.125) = 1.0 \times 10^{-14}$$

$$[H_3O^+] = 8.0 \times 10^{-14}$$

$$\boxed{pH = 13.10}$$