

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

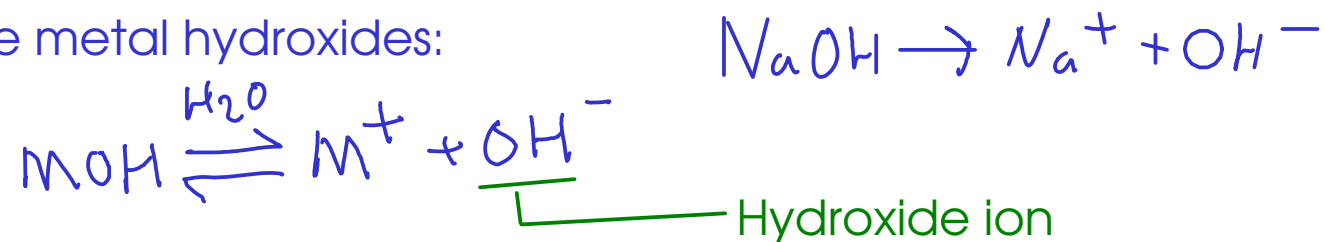


"Hydrogen ion" - doesn't really exist as a free ion in water, but a convenient simplification!

ARRHENIUS THEORY

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

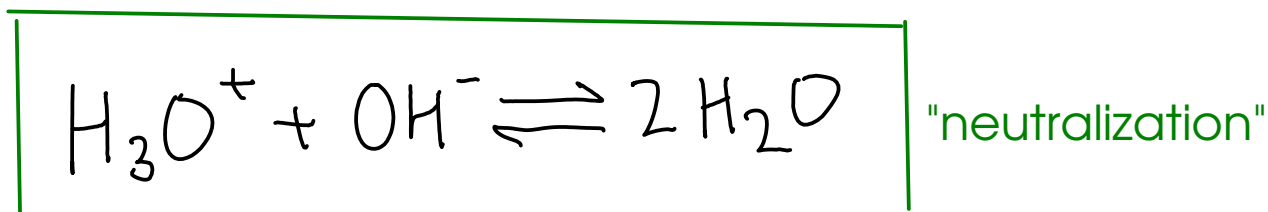
For soluble metal hydroxides:



For other Arrhenius bases:



An Arrhenius acid base reaction can be represented by:



or, using hydrogen ion instead of hydronium



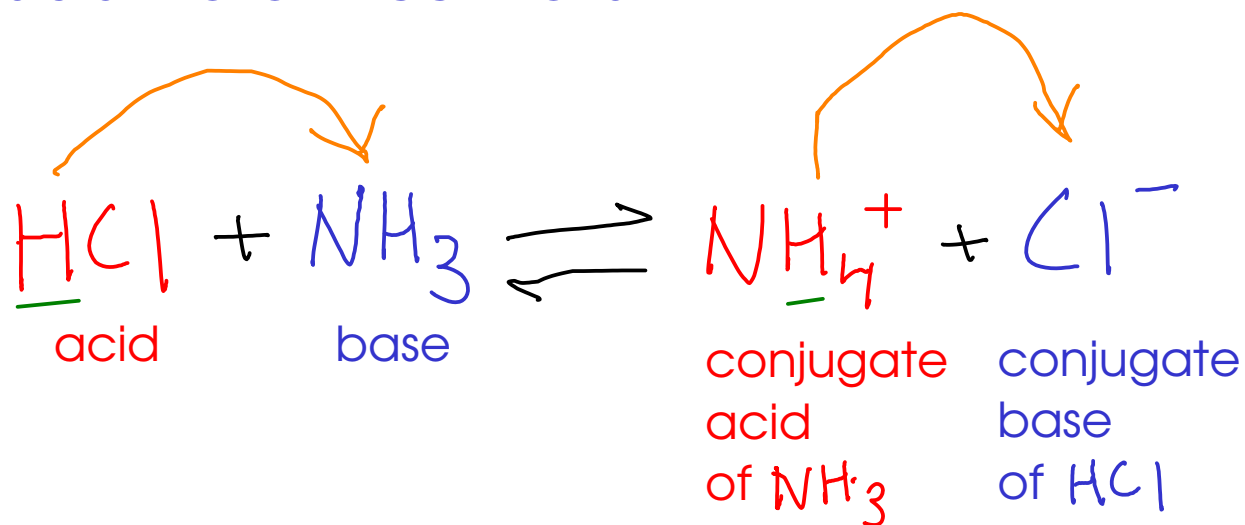
BRONSTED-LOWRY THEORY

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!

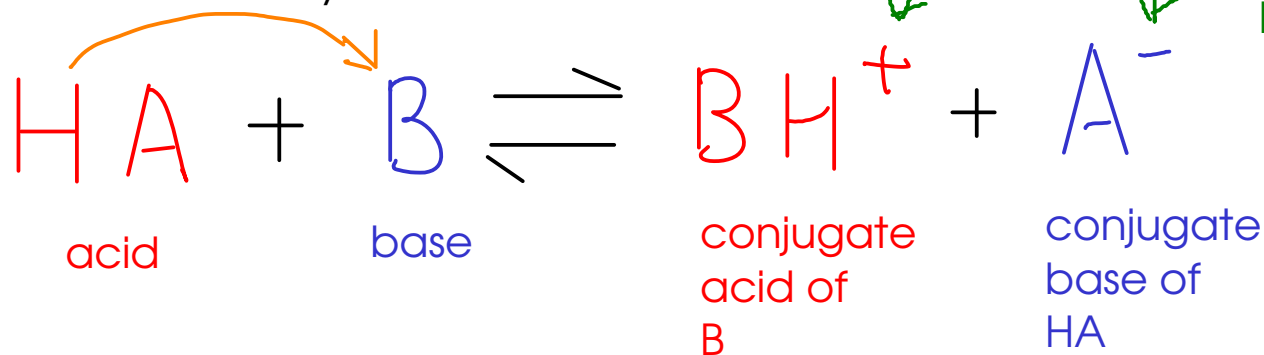
... a few examples of conjugate pairs:

Species	Conjugate
NH_3	NH_4^+
H_2O	OH^-
H_2O	H_3O^+
$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$

RED for acid

BLUE for base

A generic Bronsted-Lowrey acid-base reaction:

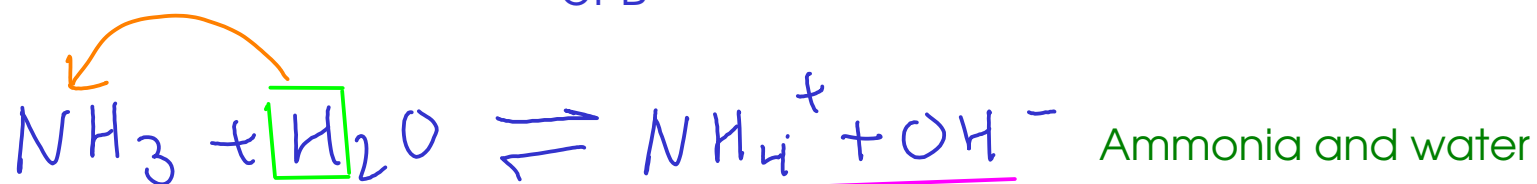
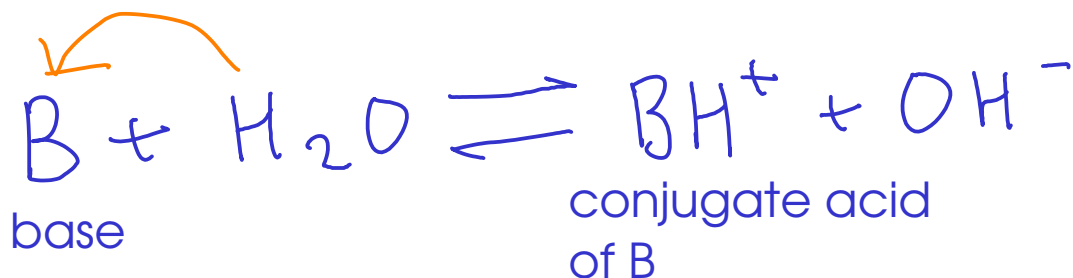
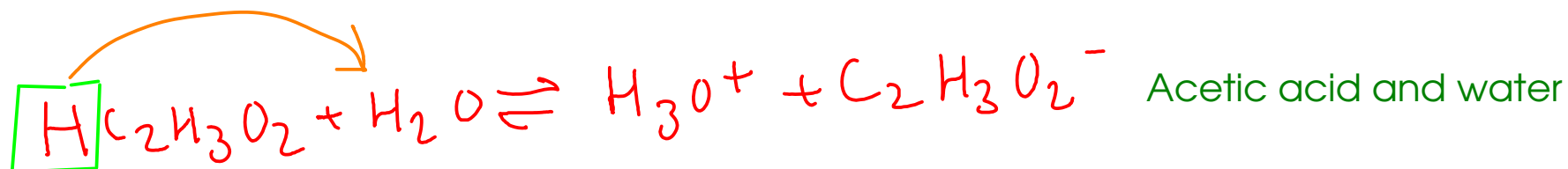
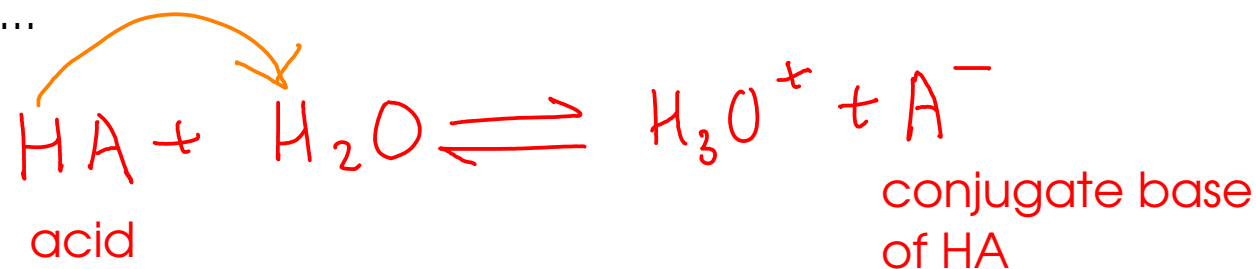


These charges are RELATIVE to whatever charge B and HA originally had...

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

BRONSTED-LOWRY THEORY

IN 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 an acid!

LEWIS THEORY

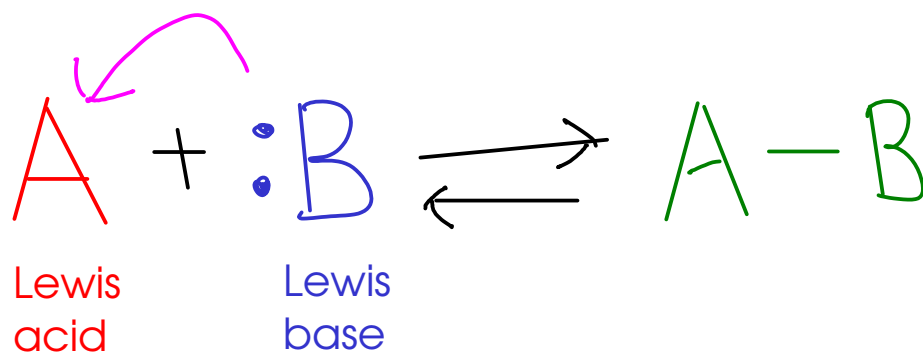
- Lewis theory treats acid-base chemistry as ELECTRON-TRANSFER chemistry involving pairs of electrons
- Lewis acid-base reactions form new covalent bonds (of interest to organic chemists!)

ACIDS are ACCEPTORS of electron pairs

... this is why some METAL IONS, even though they contain no hydrogen 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.

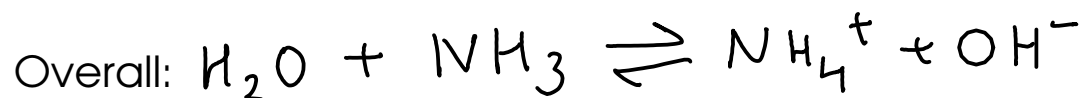
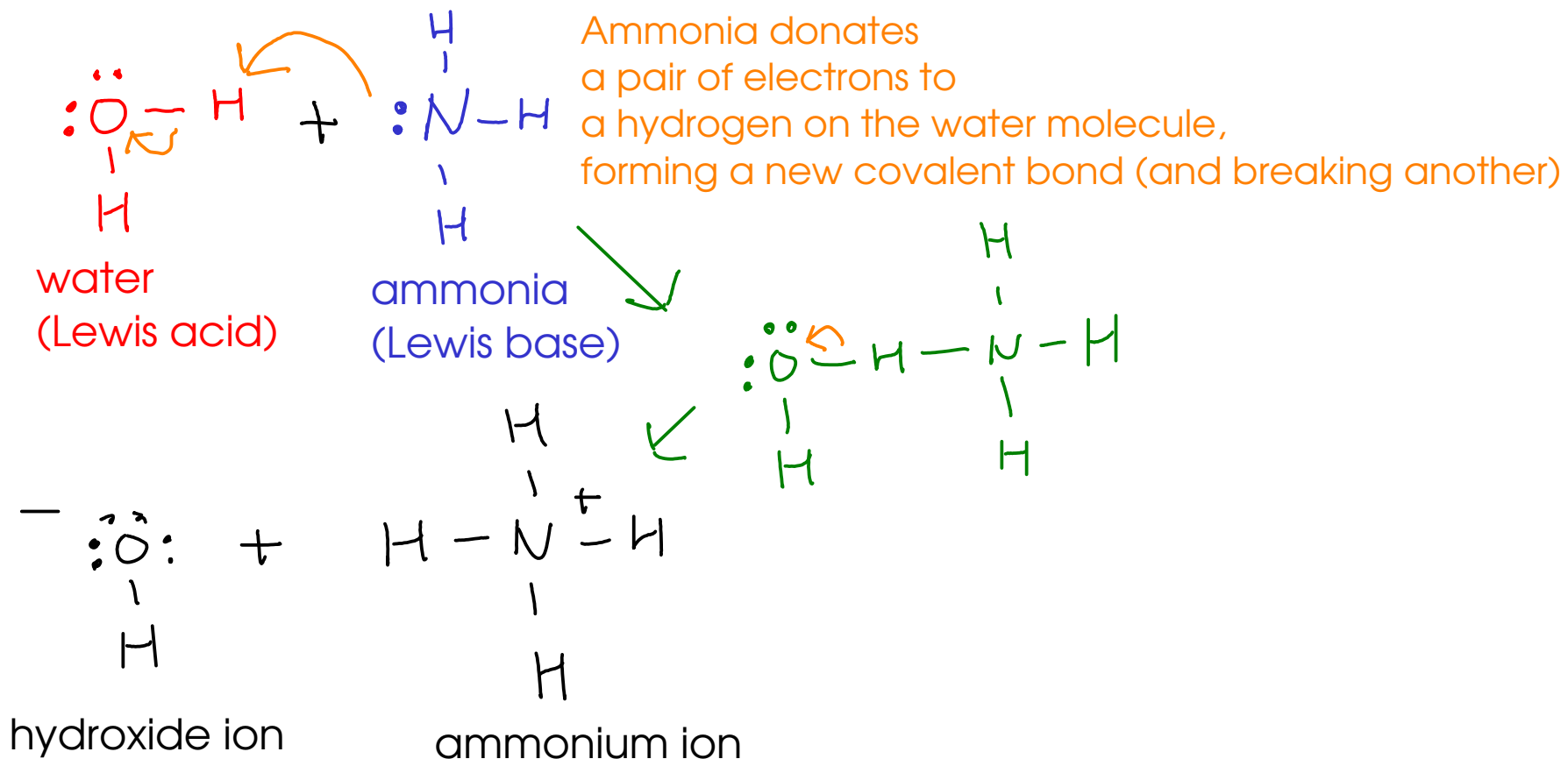
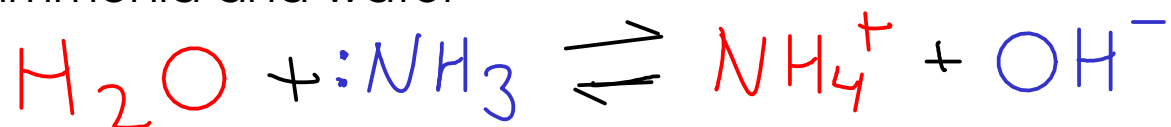
... so, Lewis bases have LONE PAIRS OF ELECTRONS in their Lewis structures



... 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



¹³⁶ COMPARING THE THEORIES

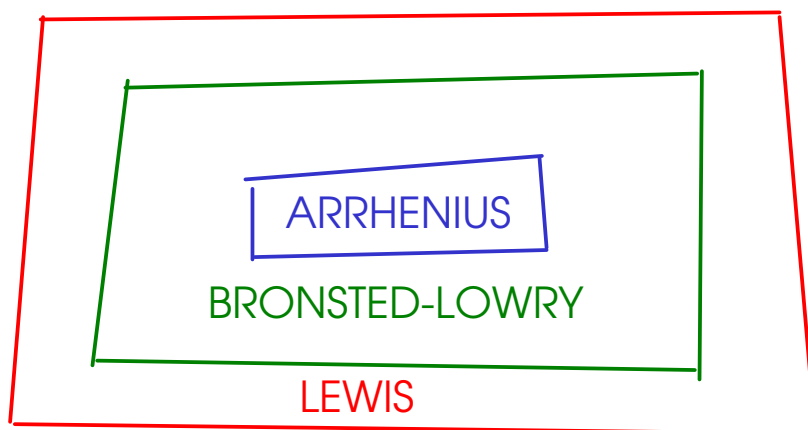
- From Arrhenius to Lewis, the definitions get broader as you go along. In other words, the later definitions include MORE SUBSTANCES under the acid/base umbrella.

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.

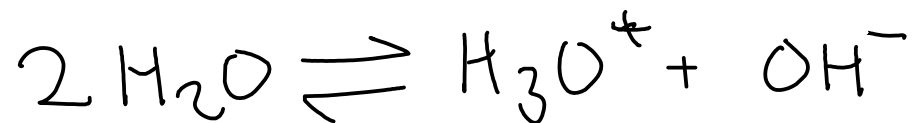
... but not all Lewis acids/bases (like the metal ions) are Bronsted or Arrhenius acids/bases.



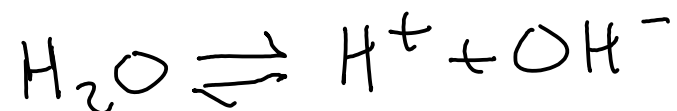
... We will primarily use the BRONSTED-LOWRY theory from this point in the course!

WATER CHEMISTRY

- Water self-ionizes!



or



This is an equilibrium reaction!

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

(X) = molar concentration of "X"

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

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

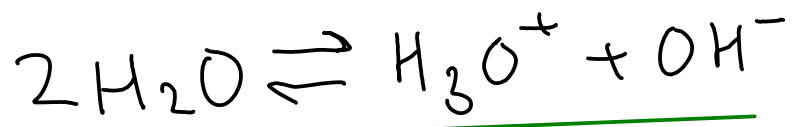
This is the value at 25C

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?



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.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$$

Solve...

Let 'x' equal the change in concentration of hydronium ion...

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

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

$$x = 1 \times 10^{-7} \text{ M} = [\text{H}_3\text{O}^+] = [\text{OH}^-]$$

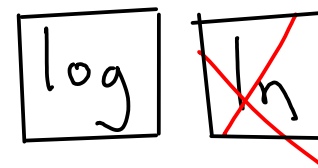
"p" NOTATION

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

- based on log base 10

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

On a calculator, use



So,

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

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

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

"p" NOTATION

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

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

becomes ...

$$pK_w = \text{pH} + \text{pOH} = 14.00$$

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 $\text{pH} = 7$, $\text{pH} = \text{pOH}$. The solution is considered NEUTRAL

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

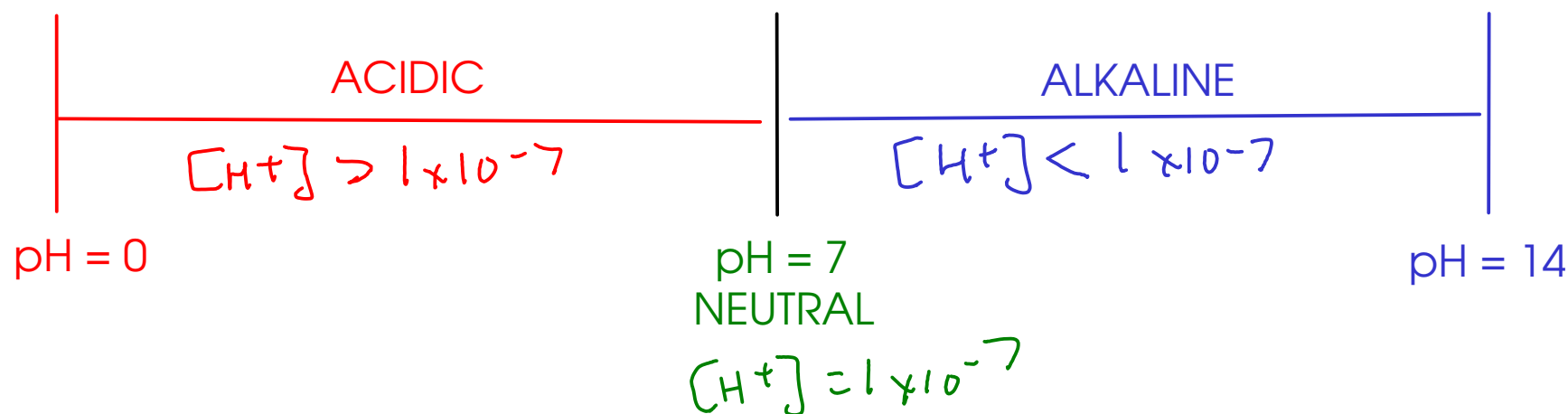
- At $\text{pH} < 7$, $\text{pH} < \text{pOH}$. The solution is considered ACIDIC

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

- At $\text{pH} > 7$, $\text{pH} > \text{pOH}$. The solution is considered ALKALINE (BASIC)

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

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

$$\text{At } 37^\circ\text{C}, \quad pK_w = 13.60$$
$$pH \text{ of neutral solution} = \underline{\underline{6.8}}$$

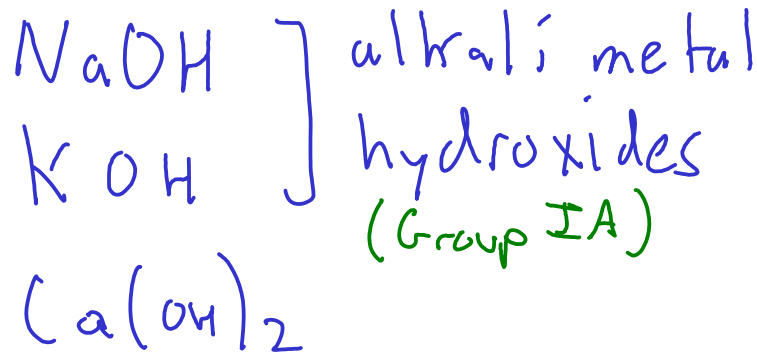
ACID-BASE EQUILIBRIUM IN WATER

- 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

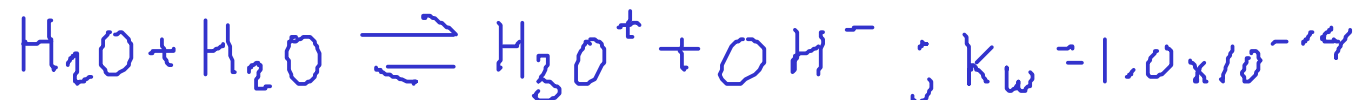


Common strong bases



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.



Consider a solution of 0.025 M nitric acid (a strong acid):



Assume that all the HYDRONIUM ION in solution comes from the nitric acid, since the hydronium ion produced by the acid suppresses water's self-ionization (Le Chateleur)

$$\text{So, } [\text{H}_3\text{O}^+] = [\text{HNO}_3]_{\text{nominal}} = 0.025 \text{ M } \text{H}_3\text{O}^+$$

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

* For logarithms, significant figures are the digits behind the decimal. The numbers in front are equivalent to the exponent of the original number

What would the HYDROXIDE ION concentration be under these conditions?

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

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

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

... this also equals the concentration of HYDRONIUM ION that water's self-ionization provides. And it's quite small compared to the acid's contribution.

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



Similar to before, we'll assume that all the HYDROXIDE ION in solution comes from the sodium hydroxide, since self-ionization of water should be suppressed by the presence of hydroxide ion.

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

We'd like to know pH so we can compare to the last example. First, find pOH

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

... Remember that pH and pOH are related:

$$\text{pH} + \text{pOH} = 14.00, \quad \text{pH} + 1.90 = 14.00$$

$$\boxed{\text{pH} = 12.10}$$

Let's check the concentration of HYDRONIUM ION, since that will give us an idea of how much water has self-ionized (remember - we assumed it was small enough to ignore compared to the sodium hydroxide):

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-12.10}$$

$$[\text{H}_3\text{O}^+] = 7.9 \times 10^{-13} \text{ M}$$

... since this also equals the amount of hydroxide ion produced by the self-ionization of water, we are justified in ignoring it compared to the hydroxide released by the base!

(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) $\text{pH} = 10.50$, $[\text{H}_3\text{O}^+] = ?$

$$10^{-\text{pH}} = [\text{H}_3\text{O}^+]$$

$$\text{so, } [\text{H}_3\text{O}^+] = 10^{-10.50} = \boxed{3.2 \times 10^{-11} \text{ M } \text{H}_3\text{O}^+}$$

B) $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$

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

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

The hydroxide ion concentration is greater than the hydronium ion concentration ... typical for BASIC solutions like this one!



The strong base will completely ionize, so all NaOH becomes OH^-

1:1 ratio of NaOH : OH^- , so

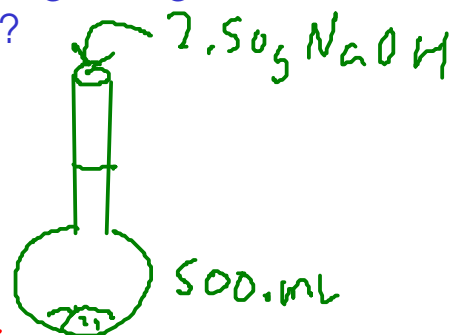
$$[\text{NaOH}]_{\text{molar}} = \boxed{3.2 \times 10^{-4} \text{ M NaOH}} \quad (0.00032 \text{ M})$$

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?

$$\text{NaOH: } 40.00 \text{ g/mol}$$

To solve this, we'll need to know the MOLAR CONCENTRATION of the sodium hydroxide:

$$M = \frac{\text{mol NaOH}}{\text{L solution}} \leftarrow 500.0 \text{ mL} = 0.5000 \text{ L}$$

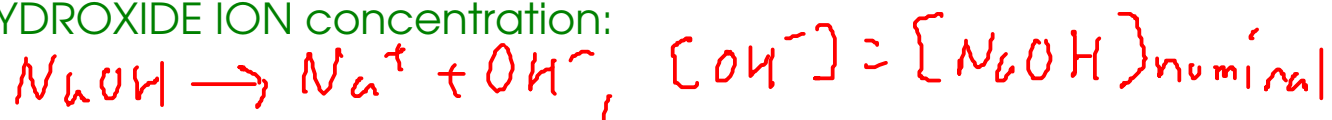


We already know volume, so we just need to find moles NaOH:

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

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

Since NaOH is a STRONG BASE, it completely ionizes in water and controls the HYDROXIDE ION concentration:



$$[\text{OH}^-] = 0.125 \text{ M}$$

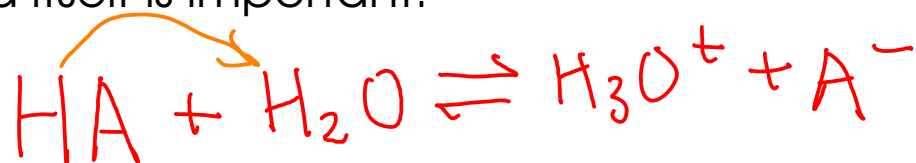
$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+](0.125) = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = 8.0 \times 10^{-14}$$

$$\boxed{\text{pH} = 13.10}$$

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



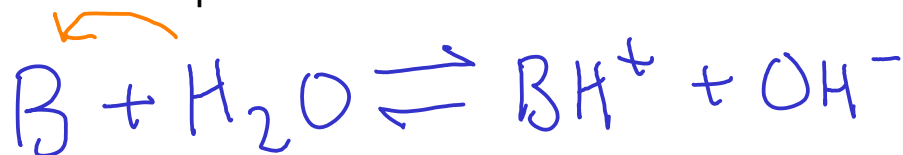
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

acid ionization constant

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



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

base ionization constant

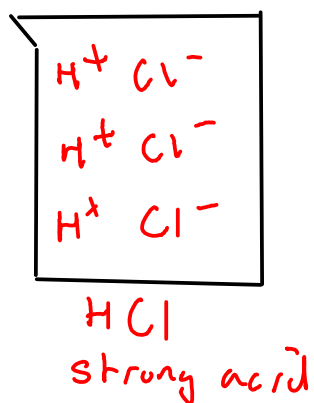
Values for K_a and K_b can often be found in data books / tables / or on the web.

In Ebbing, this data is in the appendices, on pages A-13 and A-14

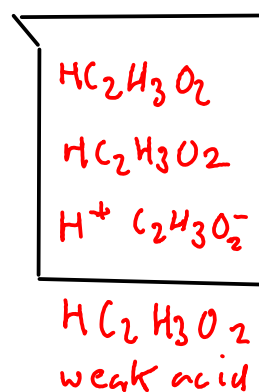
WEAK ELECTROLYTES

- 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!



VS



Fewer molecules of the weak acid ionize, so the concentration of hydrogen/hydronium ion is lower, meaning a higher pH!

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