BRONSTED-LOWRY THEORY

H$^+$ ions!

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

ACIDS are PROTON DONORS

BASES are PROTON ACCEPTORS

$$\underline{H}Cl + NH_3 \rightleftharpoons N\underline{H}_4^+ + Cl^-$$

acid

base

conjugate acid of NH_3

conjugate base of HCl

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^+
$HC_2H_3O_2$	$C_2H_3O_2^-$

RED for acid

BLUE for base

A generic Bronsted-Lowrey acid.base reaction:

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

acid

base

conjugate acid of B

conjugate base of HA

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...

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

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

$$NH_3 + \boxed{H}_2O \rightleftharpoons \underline{NH_4^+ + OH^-}$$

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

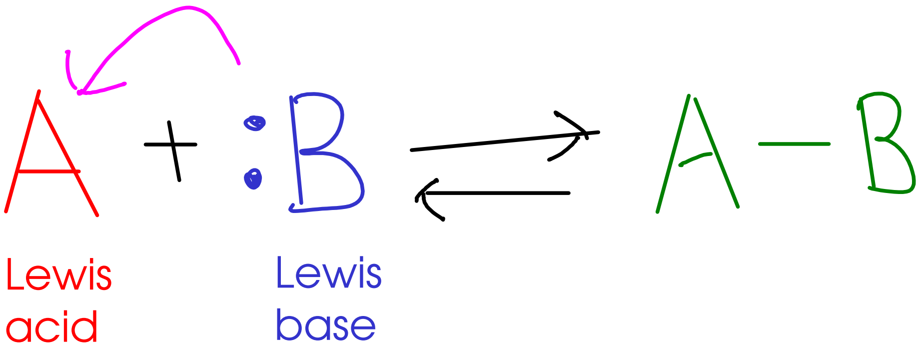
- Lewis acid-base reactions form new covalent bonds (of interest to organic chemists!)

ACIDS are ACCEPTORS of electron pairs

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

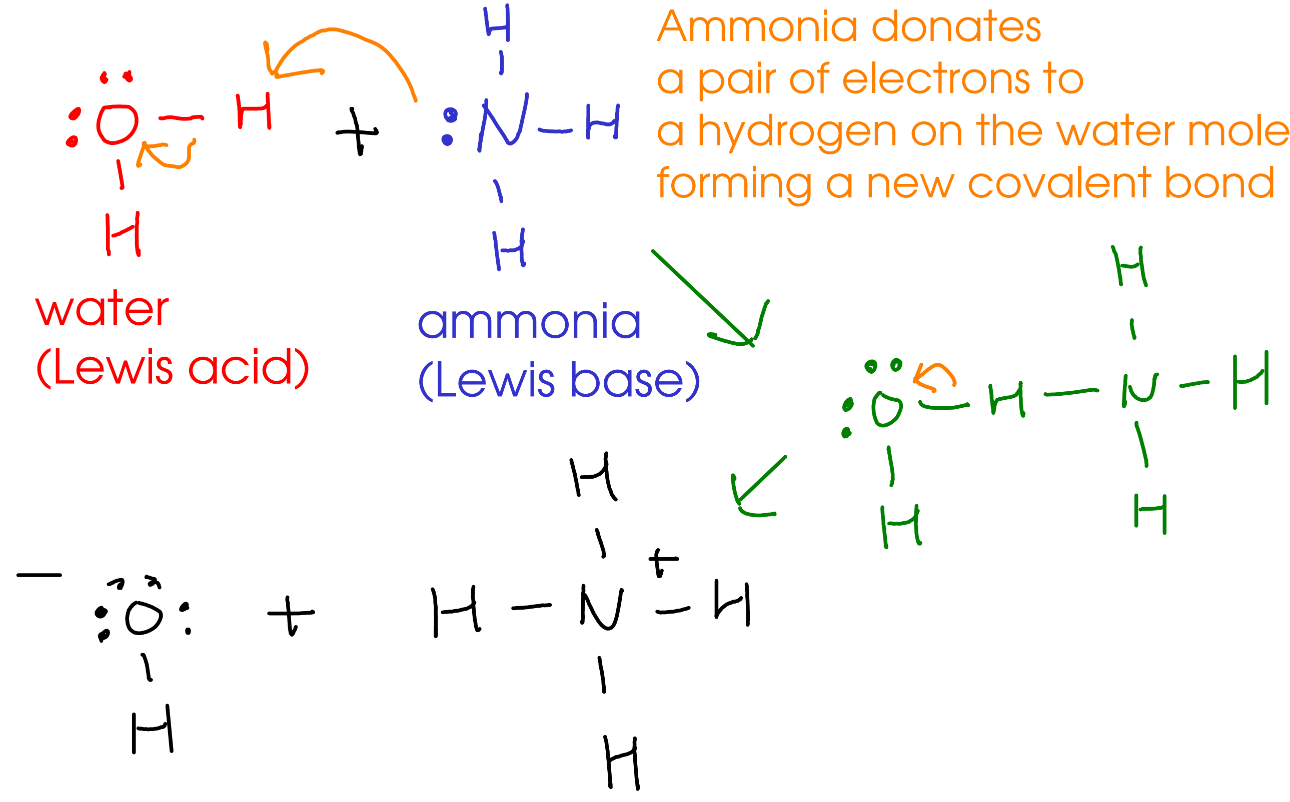


... In a Lewis acid-base reaction, electrons are donated from the Lewis base to the Lewis acid. This forms a new COVALENT BOND between the acid and the base.

LEWIS THEORY

Example: ammonia and water

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



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

water (Lewis acid)

ammonia (Lewis base)

hydroxide ion

ammonium ion

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

COMPARING THE THEORIES

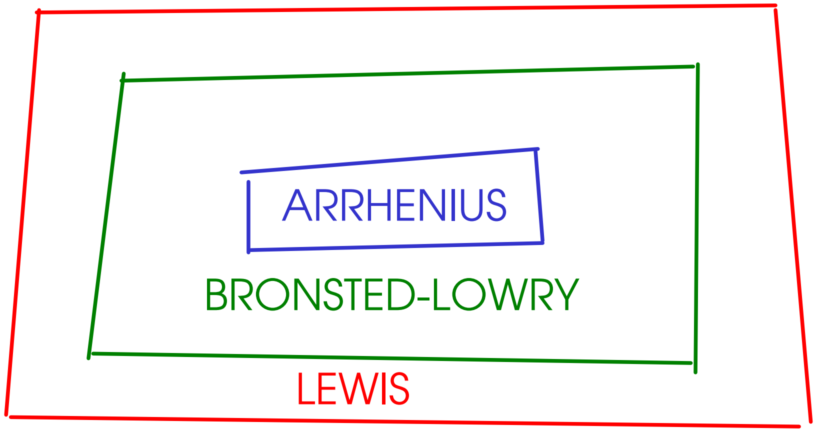
- From Arrhenius to Lewis, the definitions get broader as you go along. In other woeds, the later definitions include MORE SUBSTANCES under the acid/base umbrella.

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.

$$\boxed{K_w = [H_3O^+][OH^-] = 1.0\times10^{-14}}$$

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?

$$2H_2O \rightleftharpoons \underline{H_3O^+ + OH^-}$$

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

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

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

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

"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

log ~~ln~~

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

So,

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

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

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

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

"p" NOTATION

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

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

becomes ...

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

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, $[H^+] = [OH^-]$!

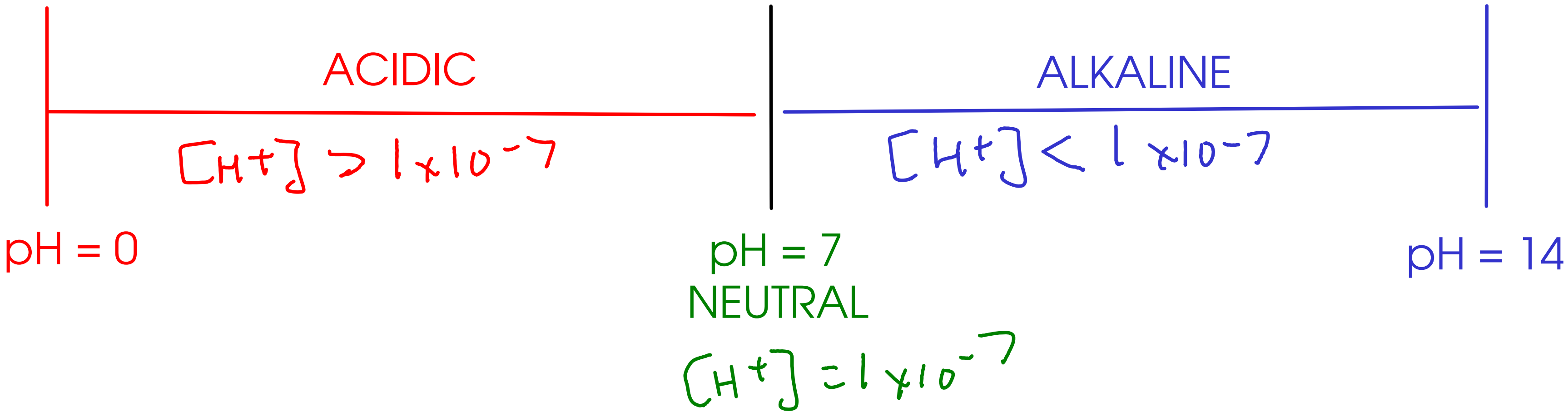
- At pH <7, pH < pOH. The solution is considered ACIDIC

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

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

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 $= \underline{\underline{6.8}}$

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

HCl

HNO_3

H_2SO_4 (only 1st proton)

HBr

HI

Common strong bases

$NaOH$] alkali metal hydroxides
KOH] (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.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \ ; K_w = 1.0 \times 10^{-14}$$

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

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

Since the presence of hydronium ion from the acid will suppress water's own ionization (Le Chateleir's principle), we'll assume that all hydronium ion in the solution comes from the acid, and that since the acid is strong the hydronium concentration will just equal the nominal concentration of the acid.

$$[H_3O^+] = [HNO_3]_{nominal} = 0.025 \text{ M } H_3O^+$$

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

* For logarithms, the significant digits are BEHIND the decimal point. The numbers in front of the decimal represent the EXPONENT of the original number, and are not significant.

Let's check our assumption. The amount of hydronium ion produced by water itself should equal the HYDROXIDE concentration of the solution!

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

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

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

... this also equals the concentration of HYDRONIUM PRODUCED BY WATER ITSELF, and it's really small compared to the 0.025M produced by the acid!