ACID/BASE EQUILIBRIUM

- Several scientific theories exist that define acid-base chemistry

- 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"!

FOUR ACID-BASE THEORIES IMPORTANT TO ANALYTICAL CHEMISTS

① Arrhenius theory

② Solvent systems theory

③ Bronsted-Lowry theory

④ 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

$$HA + H_2O \rightleftharpoons \underline{H_3O}^+ + A^-$$

Hydronium ion

or, for simplicity: $HA \xrightleftharpoons{H_2O} \underline{H}^+ + A^-$

"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:

$$MOH \xrightleftharpoons{H_2O} M^+ + \underbrace{OH^-}_{\text{Hydroxide ion}}$$

For other Arrhenius bases:

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

An Arrhenius acid base reaction can be represented by:

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

"neutralization"

or, using hydrogen ion instead of hydronium

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

SOLVENT SYSTEMS THEORY

- Typically used for systems where water is NOT the solvent!

ACIDS are substances that ionize to increase the concentration of the CATION of the solvent

BASES are substances that ionize to increase the concentration of the ANION of the solvent

Compare this to Arrhenius theory! What if we apply solvent system theory to a system with water?

$$\underbrace{H_2O \rightleftharpoons H^+}_{\text{cation of solvent}} + \underbrace{OH^-}_{\text{anion of solvent}}$$

- the acid would increase H^+
- the base would increase OH^-

Familiar?

BRONSTED-LOWRY THEORY

- Bronsted-Lowry theory views acid-base reactions as PROTON (H^+) TRANSFER reactions!

ACIDS are PROTON DONORS

BASES are PROTON ACCEPTORS

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

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!

BRONSTED-LOWRY THEORY

IN WATER...

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

acid

conjugate base
of HA

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

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

base

conjugate acid
of B

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

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

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!)

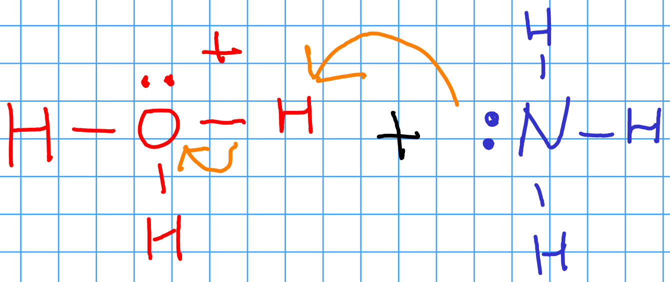
ACIDS are ACCEPTORS of electron pairs

BASES are DONORS of electron pairs

LEWIS THEORY

Example: ammonia and hydrochloric acid

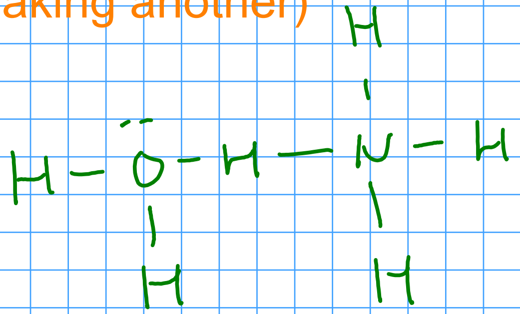
$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

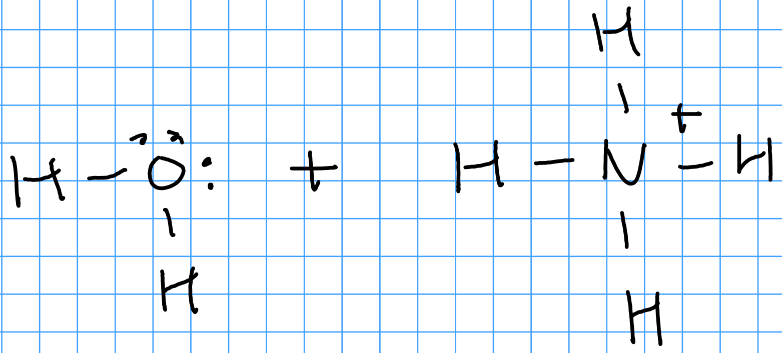


hydronium ion
(Lewis acid)

ammonia
(Lewis base)

Ammonia donates a pair of electrons to a hydrogen on hydronium ion, forming a new covalent bond (and breaking another)





water

ammonium ion

overall,

$$H_3O^+ + NH_3 \rightleftharpoons NH_4^+ + H_2O$$

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.

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

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?

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

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.

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

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

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

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

"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,

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

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

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

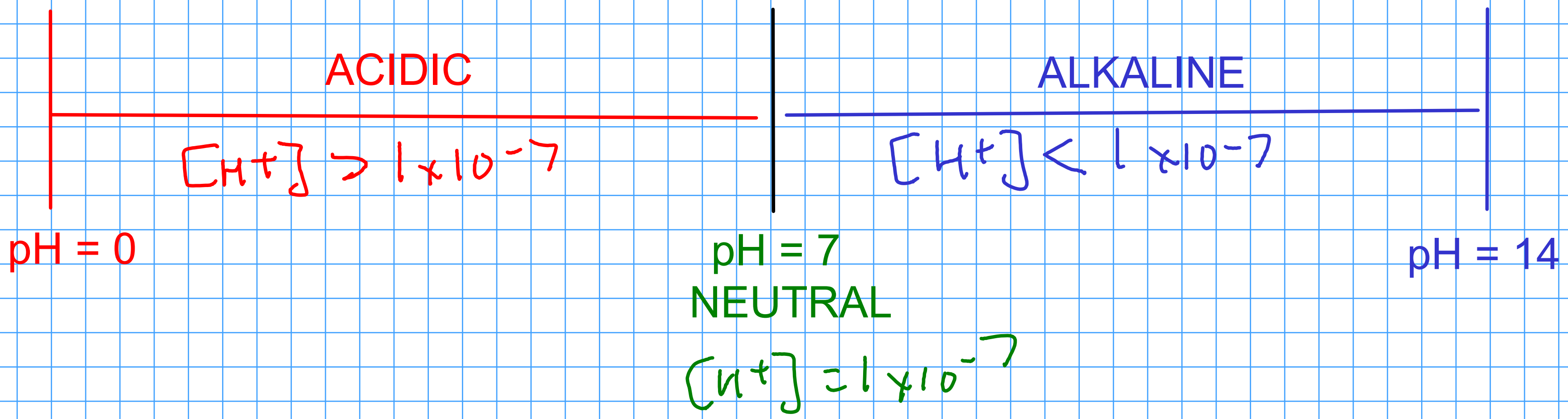
- At pH <7, pH < pOH. The solution is considered ACIDIC

Also, $[H^+] > [OH^-]$!

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

Also, $[H^+] < [OH^-]$!

The pH scale...



ACIDIC

$[H^+] > 1\times10^{-7}$

ALKALINE

$[H^+] < 1\times10^{-7}$

pH = 0

pH = 7

NEUTRAL

$[H^+] = 1\times10^{-7}$

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

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 $\underline{M}$ HNO_3

Assume all H_3O^+ comes from acid!

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

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

$$pH = 1.\underbrace{60}$$

significant digits are after decimal!

$$pOH = 14.00 - pH$$

$$pOH = 12.40$$

Consider 0.0125 $\underline{M}$ NaOH

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

Assume all OH^- comes from base

$KOH \rightarrow K^+ + OH^-$

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

$pOH = 1.90$

$pH = 14.00 - pOH$

$pH = 12.10$

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

$[OH^-]$ from H_2O

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

$\left.\begin{array}{l} NaOH \\ KOH \end{array}\right]$ alkali metal hydroxides

$Ca(OH)_2$

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

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

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

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

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!

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

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

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 basesolution 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!

ignore H_2O equil.

	initial	change	at equilibrium
$[H_3O^+]$	$= 0$	$+X$	X
$[NO_2^-]$	$= 0$	$+X$	X
$[HNO_2]$	$= 0.100$	$-X$	$0.100 - x$

$X =$ $[HNO_2]$ that dissociates

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

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

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

Quadratic equation!

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

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

$$\Big\downarrow$$

Assume that x << 0.100 (this is a weak acid)

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

$$x^2 = .000051$$

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

$$pH = \boxed{2.15}$$

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!