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

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!



ARRHENIUS THEORY

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

For soluble metal hydroxides:

$$N_{\alpha}OH \rightarrow N_{\alpha}^{+} + OH^{-}$$

 $M_{\alpha}OH \rightarrow N_{\alpha}^{+} + OH^{-}$
 $M_{\alpha}OH \rightarrow N_{\alpha}^{+} + OH^{-}$
Hydroxide ion
For other Arrhenius bases:
 $B + H_{2}O \rightarrow BH^{+} + OH^{-}$ $e_{Y}: MH_{3}$

An Arrhenius acid base reaction can be represented by:

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

or, using hydrogen ion instead of hydronium

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

Ht ions





A CONJUGATE PAIR is an acid and a base that differ by a proton!



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



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! e_X , $A_g(NH_3)_2^+$

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

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Example: ammonia and water

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



¹²⁸ 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 <u>BRONSTED-LOWRY</u> theory from this point in the course!

WATER CHEMISTRY

- Water self-ionizes! $2 H_2 O \rightleftharpoons H_3 O^{+} O H^{-}$ or $H_2 O \rightleftharpoons H^{+} + O H^{-}$ This is an equilibrium reaction!

$$K = \frac{[H_2 O^+][OH^-]}{[H_2 O]^2}$$
(X) = molar concentration of "X"

In aqueous solution, (H_2^0) is essentially constant, so we roll that into K.

$$K_{w} = \left[H_{3}O^{+}\right]\left[OH^{-}\right] = 1.0\times10^{-14}$$
This is the value at 25C

- 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.
$$K_w = [H_3O^+][OH^-] = |\chi|O^{-14}$$
Solve...
Let 'x' equal the change in concentration of hydronium ion...
$$(\chi)(\chi) = |_{-D} \chi|O^{-14}$$

$$\chi^2 = |\chi|O^{-14}$$

$$\chi^2 = |\chi|O^{-14}$$

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$$\chi^2 = |\chi|O^{-14}$$

"p" NOTATION

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



"p" NOTATION

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

becomes ...

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 $A(s_0, CH^+) \ge [OH^-]$.

- At pH <7, pH < pOH. The solution is considered ACIDIC Also, $[N^{+}] > [ON^{-}]$.

The pH scale...

$$\begin{array}{c|c} ACIDIC & ALKALINE \\ \hline CH+] > 1 \times 10^{-7} & \Box H+] < 1 \times 10^{-7} \\ pH = 0 & pH = 7 \\ NEUTRAL \\ \hline (H+] = 1 \times 10^{-7} \end{array}$$

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

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 bases

NaOH Julkali metal KOH Jhydroxides (Group IA) (a(04)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.

$$H_{20} + H_{20} = H_{30}^{+} + OH^{-}; K_{w} = 1.0 \times 10^{-14}$$

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

 $HNO_{3} + H_{2}O \longrightarrow H_{3}O^{+} + NO_{2}^{-}$

Assume that all hydronium ion in solution comes from the nitric acid, since the presence of the acid should suppress the self-ionization of water.

$$50, CH_30^+] = CHN033nominal =
 $\rho H = -\log_{10}(0.025) = 1.60$$$

What would the HYDROXIDE concentration be under these conditions? $[4_{3}0^{+}] \{0_{4}-] = 1.0 \times 10^{-14}$ $(0.025) \{0_{4}-] = 1.0 \times 10^{-14}$ $(0.025) \{0_{4}-] = 4.0 \times 10^{-13}$ M * 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.

... 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!