

# Stuff

- Workshop Info: the two Thursday 10am sessions (CRN 65530 and 65531) will be combined into one single session and it will still be meeting on Thursday at 10am but the location has moved to Meetro coffee shop (next the Hoffman Hall).
- Winter Finals can be picked up in my office
- You can still access all of your scores from the winter on the web-just until Thurs.
- Syllabus contains all of the info. The course structure is identical to the first two quarters
- First HW assignment is posted. New students-make sure you understand the operation of the system and how the points are assigned.
- Nomenclature will remain a critical aspect of the course.
- Students needing add cards signed-see me after class

# A Quick Review of the basics of acid/bases

- Refer to sec 4.3(p. 119) and 4.5(p. 123)
- Arrhenius
  - **Acid:** produces an acidic aqueous solution:  $[H^+] > [OH^-]$
  - **Base:** produces a basic aqueous solution:  $[H^+] < [OH^-]$
- Bronsted-Lowry
  - Acid: proton,  $H^+$ , donor-note it is a **cation** which is donated
  - Base: proton,  $H^+$ , acceptor
  - Proton transfer  $HA + B \rightleftharpoons A^- + BH^+$ , Again,  $H^+$  was transferred. The following is **incorrect**:
    - $HA + B \rightleftharpoons A + BH$
  - Conjugate pairs  $HA$  and  $A^-$   $B$  and  $BH^+$ -two species related by a proton.

# Identifying Acids and Bases

- You are responsible for knowing the strong species shown in Table 4.2, p. 124. In addition,  $\text{HClO}_4$ , perchloric, should be added to the list of strong acids. In most cases  $\text{KOH}$  and  $\text{NaOH}$  will be the strong bases used.
- **Neutrals**-the conjugate bases of the strong, monoprotic acids are neutral. Ex:  $\text{NO}_3^-$
- **Other conjugates**: all other conjugates( of the weak species) are weak
- The formula of a chemical compound is usually presented in a fashion that indicates whether the compound has acid/base character. Proper identification is the crucial first step in analyzing acid/ base systems. You should look for the following
  - Is there a leading H? In most cases that hydrogen is acidic. Ex:  $\text{HNO}_2$ .
  - Does the compound end in  $\text{CO}_2\text{H}$ ? This is a carboxylic acid- the most common weak acid type. Ex:  $\text{CH}_3\text{CO}_2\text{H}$ .
  - Does the compound end in  $\text{NH}_x$  ( $x=0,1,2,3$ ). These are nitrogen bases, the most common type of weak bases.  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $(\text{CH}_3)_3\text{N}$
  - Ions- generally anions will be bases and cations will be acids as they are often formed by the loss (anions) and gain (cations) of  $\text{H}^+$ . That is the question you need to ask-can this ion be viewed as having been formed by the loss or gain of a proton?  $\text{ClO}_3^-$  (weak base);  $\text{C}_5\text{H}_5\text{NH}^+$ (weak acid)

# Aqueous Solutions of acids and bases

Many substances are capable of being both an acid and a base-these are called amphoteric.

Can an Arrhenius acid or base be amphoteric?

Any amphoteric substance, such as water, is capable of autoionization:



This process has an equilibrium constant,  $K_w$ , with a value of  $10^{-14}$  at room temperature

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

In pure water  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$

Assume that a substance which produces  $\text{H}^+$  is added to the water

What is the complete description of how the  $[\text{H}^+]$  and  $[\text{OH}^-]$  are affected?

What basic principle of equilibrium is at work here

## $[H^+]$ , pH, etc

- The description of an aqueous solution of an acid (or base) begins with the proper identification of the species and ends with values being assigned to seven quantities.
  - $[H^+]$ ,  $[OH^-]$ , pH, pOH,  $[HA]$  or  $[B]$ ,  $[A^-]$  or  $[BH^+]$ , % ionization
- A critical aspect of this is use of p terms, pH, pOH and sometimes pK.  $pX = -\log X$
- $pH = -\log[H^+]$ ,  $pOH = -\log[OH^-]$  and  $pK = -\log K$
- Difficulties arise in this area largely because many students have not had any formal instruction in the meaning/use of base 10 logarithms. Thus, dependence on the calculator becomes extreme—often with poor results.
- Since we will be largely dealing with aqueous solutions, where  $K_w$  is the dominant factor
  - $[H_3O^+][OH^-] = 10^{-14}$
  - $pH + pOH = pK_w = 14$

# Simplifying pH, etc

Suppose you had an aqueous solution where  $[H^+]=0.063$ . How would you determine  $[OH^-]$ , pH and pOH?

One method would be to do the following:

$$[OH^-]=10^{-14}/0.063 =1.6*10^{-13}$$

$$pH=-\log(0.062)=1.20$$

$$pOH=-\log(1.6*10^{-13})=12.8$$

Likewise, if you were told that  $pOH=4.35$ , to get the other values you might

$$pH=14-4.35=9.65$$

$$[OH^-]=10^{-4.35}=4.5*10^{-5}$$

$$[H^+]=10^{-14}/4.5*10^{-5}=2.2*10^{-10}$$

The approaches noted above will certainly work, but the student needs to be aware of the large number of keystrokes required and how easy it is to introduce an error.

There is an approach to these problems which minimizes the number of calculator operations as well as being faster and also having a number of internal checks.

In sci notation,  $[H^+] = C_A \cdot 10^{-E_A}$  and  $[OH^-] = C_B \cdot 10^{-E_B}$

If one eliminates the special cases of []s being greater than 1.00 and the coefficients of the concentrations ( $C_A, C_B$ ) being=1, there are a number of very useful simplifications which can be applied to conversions between pH, pOH, etc

- $pH = O_A \cdot M_A$   $pOH = O_B \cdot M_B$   $[H^+] = C_A \cdot 10^{-E_A}$   $[OH^-] = C_B \cdot 10^{-E_B}$
- $O_A + O_B = 13$   $E_A + E_B = 15$   $M_A + M_B = 1.00$   $C_A \cdot C_B = 10$
- $O_A = E_A - 1$   $O_B = E_B - 1$
- $M_A = \log C_B$   $C_B = 10^{M_A}$
- $M_B = \log C_A$   $C_A = 10^{M_B}$
- The critical check is that the lesser C has the larger M and the greater C the lesser M

# Solutions of strong species

For any solution, we label the concentration of the solute prior to any ionization as  $C_i$

If the species is a “strong” aqueous **acid**

Ionization is 100%

$$[\text{H}^+] = C_i$$

$$[\text{A}^-] = [\text{H}^+] \text{ (this is generally true)}$$

$$[\text{HA}] = 0$$

$$[\text{OH}^-] = K_w / C_i$$

Analogous statements can be made with regards to strong bases-just exchange the positions of  $[\text{H}^+]$  and  $[\text{OH}^-]$

## Exceptions

$\text{H}_2\text{SO}_4$ -where the second ionization contributes additional hydrogen ion

Very dilute solutions where the contribution of the autoionization of the water cannot be ignored



# Solutions of strong species

- ❖ Analogous statements can be made with regards to strong bases
- ❖ Exceptions
  - ❖  $\text{H}_2\text{SO}_4$  where the second ionization contributes additional hydrogen ion
  - ❖ Very dilute solutions where the contribution of the autoionization of the water cannot be ignored

# Weak Acids

- A weak acid HA will ionize only partially and attain an equilibrium defined by an equilibrium constant,  $K_a$
- $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$
- $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]_{\text{eq}}}$
- $[\text{H}_3\text{O}^+] = [\text{A}^-]$  and  $[\text{HA}]_{\text{eq}} = C_i - [\text{H}_3\text{O}^+]$
- $K_a = \frac{[\text{H}_3\text{O}^+]^2}{(C_i - [\text{H}_3\text{O}^+] )}$

- ✓ The preceding quadratic can be rearranged and the quadratic formula used

$$[\text{H}_3\text{O}^+] = \frac{-K_a + (K_a^2 + 4K_a C_i)^{1/2}}{2}$$

- ✓ In addition to being awkward, use of the above equation is usually unnecessary due to the Weak Acid Approximation
- ✓ If you have a programmable calculator, it is recommended that you learn how to use it to do the above computation and that you practice extensively.
- ✓ For a weak base, replace  $[\text{H}_3\text{O}^+]$  with  $[\text{OH}^-]$  and  $K_a$  with  $K_b$ .

# Weak acid Approximation

- In general, weak acids ionize to such a small extent that  $[\text{H}_3\text{O}^+] \ll C_i$
- The equilibrium expression simplifies to:
  - $K_a = [\text{H}_3\text{O}^+]^2 / C_i$
  - $[\text{H}_3\text{O}^+] = (K_a * C_i)^{1/2}$
  - The resultant  $[\text{H}_3\text{O}^+]$  is considered valid if it is less than 5% of  $C_i$
  - In most cases, the weak approximation yields a satisfactory result and a more exact solution is not needed. In any problems assigned on exams or quizzes, the **weak approx must be attempted** before an exact solution is calculated.
- An analogous treatment can be used for weak bases, replace  $[\text{H}_3\text{O}^+]$  with  $[\text{OH}^-]$  and  $K_a$  with  $K_b$ .

# General Scheme for acid/base solutions

- Identify the species-neutral or strong
  - neutral (a salt of chloride, bromide, iodide, nitrate or perchlorate ion)-pH=7 and you're done
  - strong acid:  $[H^+] = [A^-] = C_i$  and then determine the values of the other 5 quantities
  - strong base  $[OH^-] = C_i$  and then determine the other 5 quantities. You only have 6 total here, since these solutions are prepared from salts of  $OH^-$  so there is no B, per se.
- If weak
  - be very careful about whether it's an acid or base-get the appropriate K value
  - try the weak approx-this is always required
  - if the weak fails-use the quadratic
  - make certain that you don't transform a base into an acid in the middle of the problem
  - once the  $[H^+]$  or  $[OH^-]$  is determined-get the other 6 quantities