Probably Worth Knowing

- HW database reset and new assignment posted. Not due until Thurs (4/19) which is also Ex 2 date.
- Exam 2 will cover the last little bit of Kinetics, all of equilibrium and all of acids and base material covered this week. We will probably not finish this set of notes this week.
- Lab report due this week consists of the flow diagram for the unknown (done professionally), identity of unknown and answers to the question.

Recognizing conjugates

- Keep in mind that in this course all of the weak acids and bases will be drawn from the tables which were distributed and will follow the tables’ formatting and naming.
- The conjugate of a weak monoprotic acid will be an anion. It will usually be shown or named as a sodium or potassium salt.
  - If the formula of the conjugate is given, it should be easily found in the table
  - If the name of the conjugate is given then you have to rely on your nomenclature skills. The anions of carboxylic acids are named by replacing -ic by ate. Acetic acid become acetate and would be called named as either sodium or potassium acetate.

Aqueous Solutions of acids and bases

The initial discussions will all involve aqueous solutions. All acid/base properties have an implied “aqueous” in them. HCl is a strong “aqueous” acid.

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:

\[ 2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq) \]

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

\[ K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14} \] (why no \(\text{H}_2\text{O}(l)\))

In pure water \([\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14} \text{ M}\)

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
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.

- \([H^+], [OH^-], pH, pOH, etc\)

- This follows from the general hydrolysis reaction noted earlier.

- HA(B) + H\(_2\)O \(\rightarrow\) A\(^-\)(B\(^+\)) + H\(_3\)O\(^+\)

- 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 are dealing with aqueous solutions, where \(K_w\) is the dominant factor

- \([H^+][OH^-] = 10^{-14}\)

- \(pH + pOH = pK_w = 14\)

### 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:

\[
[OH^-] = \frac{10^{-14}}{0.063} = 1.6 \times 10^{-13}
\]

\[
pH = -\log(0.063) = 1.20
\]

\[
pOH = -\log(1.6 \times 10^{-13}) = 12.8
\]

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

\[
pH = 14 - 4.35 = 9.65
\]

\[
[OH^-] = 10^{-4.35} = 4.5 \times 10^{-5}
\]

\[
[H^+] = 10^{-9.65} = 2.2 \times 10^{-10}
\]

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, \([H^+] = C_A \times 10^{E_A}\), and \([OH^-] = C_B \times 10^{E_B}\)

- If one eliminates the special cases of \(C\) 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:

  - \(pH = E_A, pOH = E_B, [H^+] = C_A \times 10^{E_A}\), \([OH^-] = C_B \times 10^{E_B}\)

  - \(O_A + O_B = 13, E_A + E_B = 15, M_A + M_B = 1.00, C_A \times C_B = 10\)

  - \(O_A = E_A - 1, O_B = E_B - 1\)

  - \(M_A = \log C_A, C_A = 10^{M_A}\)

  - \(M_B = \log C_B, C_B = 10^{M_B}\)

  - The critical check is that the lesser \(C\) has the larger \(M\) and the greater \(C\) the lesser \(M\)
A Little Practice

<table>
<thead>
<tr>
<th>[H+]</th>
<th>[OH⁻]</th>
<th>pH</th>
<th>pOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td></td>
<td>11.67</td>
<td></td>
</tr>
<tr>
<td>6.7×10⁻⁴</td>
<td></td>
<td>5.45</td>
<td></td>
</tr>
</tbody>
</table>

Comments on pH, etc

- You are given pH=11.26 and asked for [H⁺]. You do the conversion and get the following answer(s). Do you understand logs sufficiently to identify the correct result?
  - 1.82×10⁻¹¹
  - 5.48×10⁻¹²
  - 2.4×10⁻¹²
  - 6.9×10⁻¹³
- What caused the incorrect results?
- What is 10⁻¹ ⁄₂ and what is its log?

Solutions of strong species

The defining characteristic of a strong aqueous acid or base is that it ionizes completely. For any solution, we label the concentration of the solute prior to any ionization as Cᵢ. If the species is a "strong" aqueous acid, ionization is 100%:

- [H⁺] = Cᵢ
- [A⁻] = [H⁺] (this is generally true from the stoichiometry)
- [HA] = 0
- [OH⁻] = Kw/Cᵢ—why is this true?

Analogous statements can be made with regards to strong bases—just exchange the positions of [H⁺] and [OH⁻].

Exceptions

- H₂SO₄, where the second ionization contributes additional hydrogen ions
- Very dilute solutions where the contribution of the autoionization of the water cannot be ignored
Quick Examples

- Provide complete treatments of the following:
  - 0.025M $\text{HNO}_3$
  - $6.7 \times 10^{-4}$ M potassium nitrate
  - 0.18M sodium hydroxide

Weak Acids

- A weak acid HA will ionize only partially and attain an equilibrium defined by an equilibrium constant, $K_a$.

  \[ \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \]

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

  \[ [\text{H}_3\text{O}^+]_{\text{eq}} = [\text{A}^-]_{\text{eq}} \text{ and } [\text{HA}]_{\text{eq}} = C_i - [\text{H}_3\text{O}^+] \]

  The "eq" subscripts are here only for effect. Acid/base equilibria are established instantaneously and it is understood that all concentrations are equilibrium ones. Thus, "eq" will not be used from hereon.

  \[ K_a = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}^2}{(C_i - [\text{H}_3\text{O}^+]_{\text{eq}})} \text{-note the difference here from the analogous equation dealing with strong species.} \]

- The preceding quadratic can be rearranged and the quadratic formula used
  \[ [\text{H}_3\text{O}^+]_{\text{eq}} = \frac{-K_a \pm \sqrt{K_a^2 + 4K_aC_i}}{2} \]

  In addition to being awkward, use of the above equation is usually unnecessary due to the Weak Acid Approximation-coming soon.

  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 $[\text{OH}^-]$, $[\text{A}^-]$ with $[\text{BH}^+]$ and $K_a$ with $K_b$. 
### Weak Acid Approximation

- In general, weak acids ionize to such a small extent that \([H_3O^+] \ll C_i\).
- The equilibrium expression simplifies to:
  \[K_a = [H_3O^+]/C_i\]
  \[[H_3O^+]^2/(K_a C_i)^{1/2}\]
- The resultant \([H_3O^+]\) 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 \([H_3O^+]\) with \([OH^-]\) 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(s)? and you’re done
  - Strong acid: \([H^+]=\sqrt{C_i}\) 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, you will always have the Ka table—be alert for conjugates
  - 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

### Solutions

- **1.25 \times 10^{-2} M acetic acid**
  - Weak acid \(K_a=1.8 \times 10^{-5}\)
  - WA approx \([H_3O^+]^2/(C_i)=1.25 \times 10^{-2} \times 1.8 \times 10^{-5} \ll 4.7 \times 10^{-5}\)
  - Checking: 5% of \(C_i=0.05 \times 1.25 \times 10^{-2}=6.2 \times 10^{-4}=4.7 \times 10^{-5}\) **valid**
  - All of the other values gotten per usual except
    - \(\%ion=[H_3O^+]^2/[C_i]=100=4.7 \times 10^{-5}/1.25 \times 10^{-2}=3.7%\)
    - \([A^-]=[CH_3CO_2^-]=C_i-[H_3O^+]=0.125-0.00047=0.124\)
- **4.5 \times 10^{-4} M NH_3**
  - Weak base \(K_b=1.8 \times 10^{-5}\)
  - WB approx yields \([OH^-]=9 \times 10^{-5}\)
  - 5% of \(C_i=2.2 \times 10^{-4}\)—this is less than the above value so the approx is **invalid**
  - The \([OH^-]\) is determined using the quadratic and then the rest of the needed quantities determined
Solutions (con’t)

• 0.65M NaHCO$_2$
  – HCO$_2^-$ is the conjugate base of H$_2$CO$_3$ (Ka=1.8*10$^{-4}$)
  – Using the relationship (Ka*Kb=Kw) Kb=5.5*10$^{-5}$
  – Problem is then completed using standard methods

• What about the following:
  • 0.25M potassium perchlorate
  • 6.3*10$^{-3}$M C$_5$H$_5$NH$^+$
  • 0.033M sodium acetate

What about Polyprotic Species?

• Looking at the $K_a$ values in the text for polyprotic species what do you see about the relative sizes of $K_a1$, $K_a2$, and $K_a3$ (if present)
• How can the observation above simplify our analysis of polyprotic species?

Polyprotic Con’t

• H$_3$A
• Three equilibria
  – H$_3$A + H$_2$O $\rightleftharpoons$ H$_2$A$^+$ + H$_3$O$^+$ $K_a$
  – H$_2$A$^+$ + H$_2$O $\rightleftharpoons$ HA$^2$- + H$_3$O$^+$ $K_a2$
  – HA$^2$- + H$_2$O $\rightleftharpoons$ A$^3$- + H$_3$O$^+$ $K_a3$
• Since it is generally true that $K_a1$ $>>$ $K_a2$ $>>$ $K_a3$, the analysis of these systems can be greatly simplified
  – All of the H$_3$O$^+$ comes from the first ionization and the weak acid approx yields [H$_3$O$^+$] $=$ [H$_2$A$^+$] $=$ [H$_3$O$^+$]$^{1/2}$
  – [H$_3$O$^+$] $=$ [H$_2$A$^+$] $=$ [H$_3$O$^+$] $=$ $K_a1$
  – [2nd conj base]=[$K_a1$]
  – Combining the above with the form of $K_a3$ (if there is a third ionization) yields
  – [A$^3$-]=$K_a2$*[$K_a3$/[H$_3$O$^+$]]
  – [3rd conj base]=$K_a2$*[$K_a3$/[H$_3$O$^+$]]
A Little More Practice

- Complete treatment of the following solutions
- 0.035M perchloric acid
- 0.10M sodium bromide
- 0.050M CH$_3$NH$_3$Cl
- 0.0030M monochloroacetic acid
- 0.040M pyridine

Acid-Base Reactions

- As noted earlier, the B-L acid base reaction has the general form
  \[ \text{HA} + \text{B} \rightleftharpoons \text{A}^- + \text{HB}^+ \quad K_{\text{B-L}} = \frac{[\text{A}^-][\text{HB}^+]}{[\text{HA}][\text{B}]} \]
- What is $K_{\text{B-L}}$ in terms of $K_a(\text{HA})$ and $K_b(\text{B})$?
- The three contributors:
  - $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+ \quad K_a$
  - $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{HB}^- + \text{OH}^- \quad K_b$
  - $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \quad K_w$
- How are these combined to yield the proton transfer and what is the form of $K_{\text{B-L}}$?
- What is $K_{\text{B-L}}$ for acetic acid and pyridine?
- There are several very useful results of this
  - Acid-base reactions run downhill to completion with the formation of the weaker acid/base pair (this is not a conjugate pair)
  - The strongest acid (base) in a given solvent system is the conjugate acid (base) of the solvent. This is called the leveling effect

Acid-base titrations

- Acid-base reactions, since they are both fast and go to completion, lend themselves to analytical applications.
- Quantitatively, the reactions are followed by precise and accurate measurements of volumes and the technique is called volumetric analysis—normally by use of a buret.
- A volumetric analysis has three components:
  - The analyte—material being analysed
  - The titrant—contained in the buret
  - An indicator—something to identify when the addition of titrant should be stopped. This is the end point.
- Its really quite simple—add the titrant until the indicator does whatever it does—usually a color change.
- The fundamental relationship is
  \[ (M^\text{titrant})V^\text{titrant} = \text{moles OH}^- \text{ in titrant} \]
- If the titration is done properly then
  \[ \text{Moles OH}^-_{\text{analyte}} = \text{moles H}^+_{\text{analyte}} \]
- The titration is the standard means for determining the equivalent weight of an acid or base. (Mass required to donate or accept one moles of H+)}
More on Krxn

- Write the equation for the reaction of nitrous acid with methylamine. What is K for this reaction?
  \[ \text{HNO}_2 + \text{CH}_3\text{NH}_2 \rightleftharpoons \text{NO}_2^- + \text{CH}_3\text{NH}_3^+ \]
  \[ K_{\text{rxn}} = K_a \cdot K_b / K_w \]
  \[ (4 \times 10^{-4}) \cdot (4.38 \times 10^{-4}) / (10^{-14}) = 1.7 \times 10^{7} \]
- Did this reaction run downhill to completion?
- \( K_a \) for \( \text{CH}_3\text{NH}_3^+ = 2.3 \times 10^{-11} \) – it’s a weaker acid than nitrous
- \( K_b \) for \( \text{NO}_2^- = 2.5 \times 10^{-11} \) – it’s a weaker base than methylamine.
- What about HOI + aniline?
- Write a "generic reaction" for acids and bases with protic solvents and use it to explain the leveling effect.

Why 5% (or maybe 10%) is valid

<table>
<thead>
<tr>
<th>( K_a )</th>
<th>( C_i )</th>
<th>Approx</th>
<th>Check</th>
<th>Exact</th>
</tr>
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<tbody>
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</table>

The Titration Curve-acid with base

[pH vs. vol Base Graph]

- pH
- Equiv Point
- Buffer Region
• Titrating a base with an acid yields the expected “reversed” curve. Polyprotic can yield multistep curves

Buffers

• The $K_a$ expression can be readily rewritten in the following form, known as the Henderson-Hasselbach Equation

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

• In addition to its utility in analyzing buffers, the above equation does point out the central nature of the base/acid ratio in determining the pH of “weak” solutions
• The treatment of buffers breaks down neatly into two categories: preparation and properties

Buffer and Titration Curves

• The behavior of buffers is readily explained by examination of a titration curve
Buffer Preparation

• It should be apparent from the pH graph and from the discussion of titration curves that the closer the pK<sub>a</sub> of the weak acid to the desired buffer, the more effective the buffer will be. In fact, the condition pH=PK<sub>a</sub> is often termed the optimum buffer point.

• In selecting the acid/base pair to be used as a buffer, choose an acid whose pK<sub>a</sub> is close to the desired pH. Try to limit your choices to monoprotic acids. Be aware that you can use the conjugate acid of a weak base to make your buffer. If you are using a table of K<sub>a</sub>'s, the exponent should be one more than the order of the desired pH.

• From an experimental standpoint, titrating the acid to the desired pH, using a high quality pH meter is an excellent way to prepare a buffer solution.

• It should be clear that since it is the base/acid ratio, not the actual [acid] or [base] there is any infinite number of possible combinations to get a given pH.

• Sample problem 1: How would you prepare a buffer whose pH is 4.00?
  - Formic acid (K<sub>a</sub>=1.8*10^-4, pK<sub>a</sub>=3.74) is a good choice
  - pH=pKa + log[Base]/[Acid] => .26=log[base]/[acid]
  - [base]/[acid]=1.82
  - For simplicity, we’ll set [acid]=1.00M and, therefore, [base]=1.82M.
  - In general, in this sort of analysis on exams or quizzes it will be permissible to set [acid]=1.00M.

• Sample problem 2: What is the pH of a solution of wherein [acetic acid]=0.50M and [acetate]=0.30M?
  - pH=pKa + log[base]/[acid] = 4.74+log(0.30/0.50)=4.52

• What acid/base pair is appropriate for the following pHs: 2.8, 3.5, 5.1

Buffer Properties

• Buffers resist changes in pH upon dilution or addition of a strong acid or base.

• Dilution-since diluting the solution changes all of the concentrations, but does not change the ratio [base]/[acid], the pH is not affected.

• What chemical reaction occurs when you add H<sup>+</sup> or OH<sup>-</sup> to a buffer solution and what concentrations are changed?

• How to address a problem of the type “An acetic acid buffer(pKa=4.74) has [HA]=1.00 and [A<sup>-</sup>]=1.10M. What would be the new pH after each of the following. In each of these, a fresh sample of buffer is used.”
  - a) 50mL of water is added to 50mL of buffer
  - b) .50g of sodium hydroxide is added to 100mL of the buffer
  - c) 10mL of 0.10M HCl is added to 50mL of buffer

- pH=4.74+log(1.10/1.00)=4.78
  a) Does adding H<sub>2</sub>O affect the [base]/[acid]?
  b) What chemical reaction occurs when the OH<sup>-</sup> is added to the mixture?
  c) How many moles of all the species, including the hydroxide are present before the reaction?
  d) How many are present after?
  e) What is the new pH?
  c) Same questions but with 10mL of 0.10M HCl added to 50mL of buffer
Adding .50g of NaOH to 100mL of buffer
What chemical reaction occurs when the OH⁻ is added to the mixture?
CH₃CO₂H + OH⁻ → CH₃CO₂⁻ + H₂O

• How many moles of all the species, including the hydroxide are present before the reaction?
  – CH₃CO₂H = 1.00M*0.100L = 0.100 moles
  – CH₃CO₂⁻ = 1.00M*0.010L = 0.010 moles
  – OH⁻ = 0.50g/40g/mole (gfw of NaOH) = 0.0125 moles

• How many moles are present after?
  – CH₃CO₂H = 0.100 - 0.0125 = 0.087
  – CH₃CO₂⁻ = 0.110 + 0.0125 = 0.123

• What is the new pH?
  – pH = 4.74 + log(0.123/0.087) = 4.89

Adding 10.0mL of 0.10M HCl to 50 mL of buffer
What chemical reaction occurs when the H⁺ is added to the mixture?
CH₃CO₂⁻ + H⁺ → CH₃CO₂H

• How many moles of all the species, including the H⁺ are present before the reaction?
  – CH₃CO₂H = 1.00M*0.050L = 0.050 moles
  – CH₃CO₂⁻ = 1.10M*0.050L = 0.055 moles
  – H⁺ = 0.10M*0.010L = 0.0010 moles

• How many moles are present after?
  – CH₃CO₂H = 0.050 + 0.0010 = 0.051
  – CH₃CO₂⁻ = 0.055 - 0.0010 = 0.054

• What is the new pH?
  – pH = 4.74 + log(0.054/0.051) = 4.76

• To illustrate the buffer effect: calculate the pH that would result from adding the acid solution to water, instead of to the buffer.

Buffer Capacity and Optimum Buffer pH

• As noted, the optimum buffer pH is when pH = pKₐ. Such a buffer will have equal resistance to both acid and base

• In certain instances (your blood buffer), it is preferable to bias the buffer to be more resistant to acid or base

• The capacity of a buffer is the amount of acid or base needed to “overwhelm” it or remove its buffering ability. This depends on the concentrations and the volume of the buffer solution. As a general rule, the capacity could be viewed as the equivalents of base or acid needed to change the pH of one liter of buffer by one pH unit. Before actually using a buffer in the “real” world, its capacity should be known.
Buffers from conjugates of weak bases

- None of the monoprotic acids in your table has a $K_a$ with an exponent of $-6$, so they are not the best for preparing a 5.x buffer.
- However, if you examine the table of bases, you see that pyridine has a $K_b$ with an exponent of $-9$ which means that its conjugate acid will have a $K_a$ with an exponent of $-6$.
  - Thus a buffer of pH 5.x could be based upon using a mixture of either of pyridine and its conjugate acid.
- Ex: prepare a buffer of pH=5.50 using pyridine and its conjugate acid
  - $K_a$ for $C_5H_5NH^+$ = $10^{-14}/K_b = 5.5 \times 10^{-6}$
  - using standard methods it can be shown that for the pH to be equal to 5.50 $[C_5H_5N]/[C_5H_5NH^+] = 1.74$
  - Is the above result what you would have expected?

LeChatelier and Acid/base systems

- The table below illustrates % ion as a function of $C_i$ for a weak acid with a $K_a = 3.5 \times 10^{-4}$. The values shown are illustrative of the general trend observed. The exact values for a given weak acid depend on its $K_a$. Similar results would be found for a weak base. Is this what you'd expect based upon the principle of LeChatelier?

<table>
<thead>
<tr>
<th>$C_i$</th>
<th>% ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
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More LeChatelier-the Common Ion Effect

- Consider a solution of a weak acid where equilibrium has been established according to the general equation: $HA + H_2O \rightleftharpoons A^- + H_3O^+$
- What are the consequences, qualitatively, if a strong acid is added to this mixture? What is the best measure (of the seven magic things) for describing what happens in general terms?
- Does the sequence matter? That is, suppose you added the weak acid to a solution of a strong acid?
- Can the mixture be analyzed quantitatively? That is, how do you determine the % ionization for a solution which contains 0.10M HCl and 0.10M HNO$_3$?
- Under what conditions is this analysis simplified?
- Describe an analogous system for a weak base. What will the common ion be?
- How does a solution of $H_2SO_4$ represent, in a way, a common ion effect? How would you analyze a 0.10M solution of $H_2SO_4$?
Relative Strengths of Acids

• The question of why acids vary in their tendency to dissociate in water is clearly fundamental and complex. A complete analysis of this requires a relatively thorough examination of the thermodynamics of the process—most readily done by use of Hess’ law—the most beloved of all thermodynamic principles.

• What would a Born-Habertype cycle for the process \( \text{HA} + \text{H}_2\text{O} \rightarrow \text{A}^{(aq)} + \text{H}_3\text{O}^+ \) look like?

• What do you think would be the major factors that would cause variation in the relative acidities?

Acid Finale—A couple of quick details

• What is the pH of \( 2.3 \times 10^{-8} \) HCl?
  – If you just do the obvious—since it’s a strong acid
  – \([\text{H}^+] = 2.3 \times 10^{-8}\) and pH=7.64.
  – This is a basic pH (>7) but you’ve added a strong acid—so it can’t be basic!

• What’s going on here?
  – At this level of dilution the \([\text{H}^+]\) due to the autoionization of water must be considered. The treatment is as follows
  • Charge neutrality requires that \([\text{OH}^-]\times [\text{H}^+] = [\text{H}_3\text{O}^+] = 10^{-7}\)
  • \([\text{H}^+][\text{OH}^-] = 10^{-14}\) or \([\text{H}^+] = 10^{-7}\) and pH=7 (neutral)

• What is the pH of \( 0.10\text{M H}_2\text{SO}_4 \)?
  – Since the first ionization is strong, the solution can also be viewed as \(0.10\text{M HSO}_4^-\) in \(0.10\text{M H}^+\)
  – \([\text{H}^+][\text{SO}_4^{2-}] / [\text{HSO}_4^-] = \text{Ka}=1.2 \times 10^{-2}\)
  – Let \(x\) be \([\text{H}^+]\) from the second ionization
  – \([\text{H}^+][\text{H}_2\text{SO}_4] = \text{Ka}=1.2 \times 10^{-2}\)
  – Rearranging and solving the resultant quadratic yields \(x=0.001\) and \([\text{H}^+]=0.11\)
  – pH=0.96