

News of the day

- New homework assignment is posted
- Scores for first HW should be posted by Thurs
- A link has been added to the Chem 222 material for anyone wishing to review
- Some more periodic tables are on the way
- You should have your tables of K values with you for the rest of the quarter.
- Expect very frequent quizzes for a while
- I will probably not get to campus until around 3pm on Thurs. I will be here 9-3 tomorrow
- Reminder on Exam 1-it will cover material up to and including April 15

Proton transfer in general

- For the proton transfer reaction:
 - $\text{HA}(\text{aq}) + \text{B}(\text{aq}) \rightleftharpoons \text{A}^-(\text{aq}) + \text{HB}^+(\text{aq}) \quad K_{\text{rxn}} = K_{\text{a}} * K_{\text{b}} / K_{\text{w}}$
- What is K_{rxn} for:
 - $\text{HF} + \text{NH}_3 \rightleftharpoons \text{F}^- + \text{NH}_4^+$
- $K_{\text{a}} = 3.5 * 10^{-4} \quad K_{\text{b}} = 1.8 * 10^{-5}$
- $K_{\text{rxn}} = (3.5 * 10^{-4} * 1.8 * 10^{-5}) / 10^{-14} = 6.3 * 10^5$. If the initial acid and base concentrations were 0.10M, over 99.9% of the will have reacted
- Did this reaction run downhill to form the weaker acid and base?
 - K_{a} for $\text{NH}_4^+ = 5.5 * 10^{-10}$
 - K_{b} for F^- is $= 2.8 * 10^{-12}$
 - NH_4^+ is weaker than HF and F^- is weaker than NH_3 , so the reaction did run downhill.

- What about the following?
- $\text{NO}_2^- + \text{C}_6\text{H}_5\text{NH}_3^+ \rightleftharpoons$

Using K_{rxn}

- It should be clear that if either the base or acid used in a proton transfer is strong, the reaction will have a very large K value and will “go to completion”
- Since proton transfer reactions are also very fast, they can be readily used for analysis. The two critical requirements for using a reaction for analysis are completion and speed. Equilibrium and kinetics
- When one or more of the species in an analysis is measured by volume, the analysis is called “volumetric”
- Volumetric analysis using acid and bases is very common and usually called an acid-base titration
- Terms of interest: analyte, titrant, indicator, equivalent mass, equivalence point and endpoint.

Parameters in an acid-base titration

- A quantity of analyte is placed in a flask to which the indicator has been added
- Titrant of precisely and accurately known concentration is added from a buret
- Addition of titrant continued until indicator changes color-end point
- At the end point it is assumed that equivalents of acid(moles of H⁺)=equivalents of base
- Equivalent weight (mass) of an acid(base) is the mass needed to donate(accept) one mole of protons. It is either equal to or an integral dividend of the gfw.
- gews of the following: HCl ,H₂CO₃, H₃PO₄

Typical Titrations

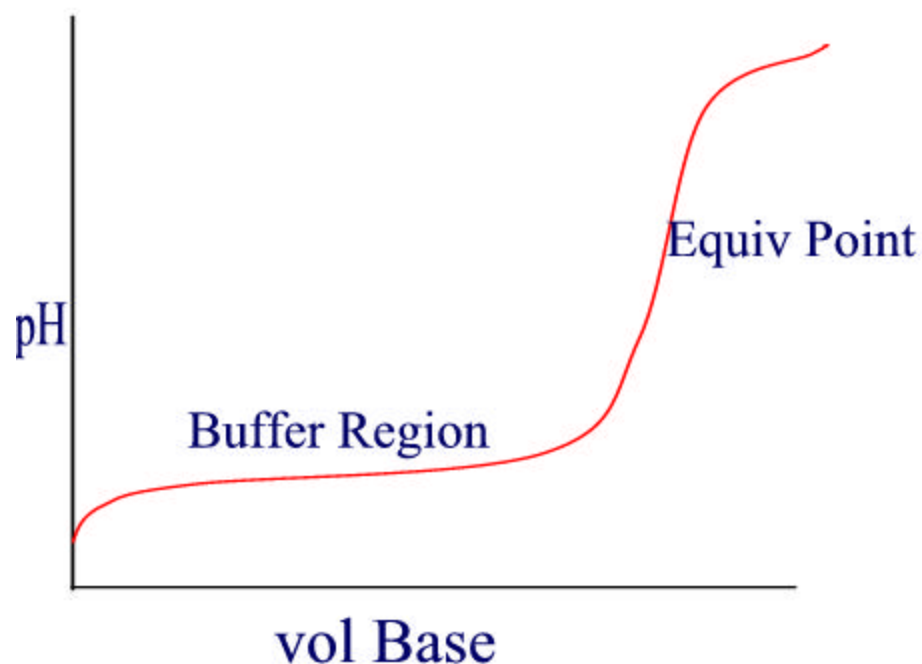
The titration of a 259mg sample of a weak acid requires 34.4mL of .100M NaOH. What is the equivalent weight of the acid?

The titration of a sample of a weak acid with an equivalent weight of 188 grams requires 24.1mL of 0.100M NaOH. What is the sample mass in mg?

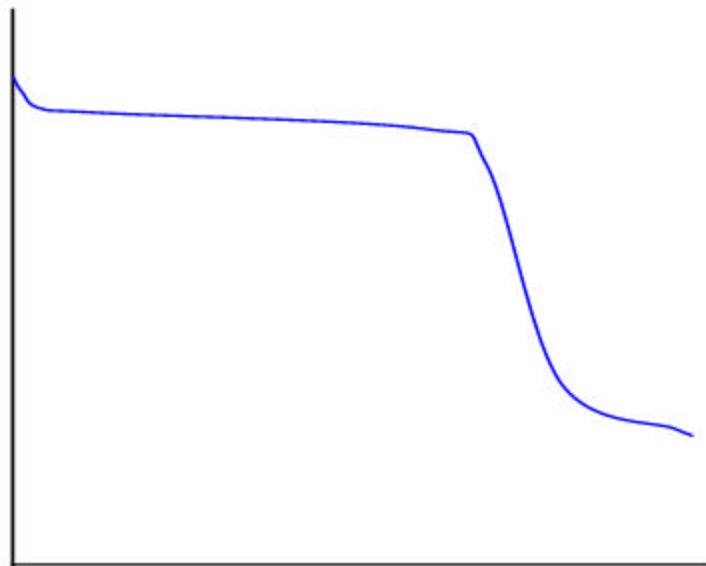
What volume in mL of .100M NaOH would be required to titrate a 0.574g sample of a weak acid with an equivalent weight of 190grams ?

Acid-Base Titration Curves

- If the pH of a solution of a weak acid is monitored as it is titrated with a strong base and the resultant data plotted, it produces what is termed a Titration Curve.
- The precise nature of the curve is dependent largely on one factor, the K_a of the acid



- Titrating a base with an acid yields the expected “reversed” curve. Polyprotic can yield multistep curves



Polyprotic acids

- Certain acids have the more than one ionizable proton-such species are termed polyprotic and will have multiple K values, normally termed K_1 , K_2 , etc.
 - For example
 - $\text{H}_3\text{PO}_4(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq}) \quad K_1$
 - $\text{H}_2\text{PO}_4^-(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq}) \quad K_2$
 - $\text{HPO}_4^{2-}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \quad K_3$
- They fall into two general classes.
 - The first type which are truly polyprotic, have all of the ionizable protons attached to the same basic unit. Examples are sulfuric and phosphoric.
 - The second are polycarboxylic, which contain multiple, independent CO_2H units.
 - The two types, in general, behave very differently with regards to the relations that exist between the successive ionization constants
 - For the first type, it is generally true that $K_1 \gg K_2 \gg K_3$ with 10^6 being typical for the degree of change-see phosphoric
 - For the second, the ionizations do not normally change by nearly that amount and ,if the groups are far enough apart on the molecule, they can be quite close in value. Ex: tartaric acid

- Calculations involving polyprotic acids will be limited to the first type. Though even this type may seem very complex, the treatment is simplified enormously due to the very large decrease in the K values, noted previously.
- Since $K_1 \gg K_2 \gg K_3$, it is reasonable to assume that only the first step contributes to the $[H^+]$ and any successive steps occur to a very limited extent. The analysis then follows the following path, using H_3PO_4 as the example.
 - $[H^+]$ is calculated as if the polyprotic species were monoprotic and the usual analysis leads to values for $[H^+]$, $[OH^-]$, and $[H_2PO_4^-]$
 - K_2 has the form $[H^+][HPO_4^{2-}] / [H_2PO_4^-]$. Since K_2 is so small, the assumption is made that it does not effect the concentrations of either $[H^+]$ or $[H_2PO_4^-]$. Since $[H^+] = [H_2PO_4^-]$ (1st ionization), $[HPO_4^{2-}] = K_2$ or, in general, the concentration of the second conjugate base = K_2
 - K_3 has the form $[H^+][PO_4^{3-}] / [HPO_4^{2-}]$. From the preceding, it can be seen that $[PO_4^{3-}] = K_2 * K_3 / [H^+]$ or, in general, the concentration of the third conjugate base = $K_2 * K_3 / [H^+]$
 - Thus, polyprotic acids of the first type, do not introduce significant additional computational issues. The only common exception is sulfuric acid where the first ionization is strong.

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 Preparation

- It should be apparent from the H-H eqn and from the discussion of titration curves that the closer the pK_a of the weak acid to the desired buffer, the more effective the buffer will be. In fact, the condition $pH=pK_a$ is often termed the optimum buffer point
- In selecting the acid/base pair to be used in a buffer, choose an acid whose pK_a is close to the needed 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_a 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 ($K_a=1.8 \times 10^{-4}$, $pK_a=3.74$) is a good choice
 - $pH-pK_a=\log[\text{base}]/[\text{acid}] \Rightarrow .26=\log[\text{base}]/[\text{acid}]$
 - $[\text{base}]/[\text{acid}]=1.82$
 - For simplicity, we'll set $[\text{acid}]=1.00\text{M}$ and, therefore, $[\text{base}]=1.82\text{M}$
 - In general, in this sort of analysis on exams or quizzes it will be permissible to set $[\text{acid}]=1.00$
- Sample problem 2: What is the pH of a solution of wherein $[\text{acetic acid}]=0.50\text{M}$ and $[\text{acetate}] = 0.30\text{M}$.
 - $pH=pK_a + \log[\text{base}]/[\text{acid}] = 4.74+\log(0.30/0.50)=4.52$

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 $[\text{base}]/[\text{acid}]$ the pH is not affected
- What chemical reaction occurs when you add H^+ or OH^- to a buffer solution and what concentrations are changed?
- How to address a problem of the type “An acetic acid buffer($\text{pK}_a=4.74$) has $[\text{HA}]=1.00$ and $[\text{A}^-]=1.10\text{M}$. 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

- $\text{pH} = 4.74 + \log(1.10/1.00) = 4.78$
- a) Does adding H_2O affect the $[\text{base}]/[\text{acid}]$?
- b) What chemical reaction occurs when the OH^- is added to the mixture?
 - How many moles of all the species, including the hydroxide are present before the reaction?
 - How many are present after?
 - What is the new pH?
- c) same series of questions as above

Buffer Capacity and Optimum Buffer pH

- As noted, the optimum buffer pH is when $\text{pH}=\text{pK}_a$. 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.