

Of interest-perhaps

- Quiz 1 scores are posted. Please check them and verify that your secret code is correct
- The six common strong acids for which you are responsible are
 - HCl-hydrochloric
 - HBr-hydrobromic
 - HI-hydroiodic
 - HNO₃-nitric
 - HClO₄-perchloric
 - H₂SO₄-sulfuric
- New students-see me for syllabus

pH, etc-the special cases

- $[H^+] > 1$
 - the pH will be negative
 - $O_A = -E_A$ –realistically this will most likely be 0, as cases where $[H^+] > 10$ are only possible in extremely concentrated solutions of strong acids where even using molarity as a measure is not valid and the elimination of H_2O from the K expression is no longer correct.
 - $M_A = -\log C_A$
 - $M_A + M_B = 0$ $M_B = \log C_A$ curious, but true
 - The other rules hold
 - $C_B = 10/C_A$
 - $E_A + E_B = 15$; Since $E_A = 0$, $E_B = 15$
 - $O_B = 14$
- What are pH, etc if $[H^+] = 3.4$?
 - $pH = -\log 3.4 = -.53$
 - $[OH^-] = 2.9 \times 10^{-15}$ $pOH = 14.53$
- An analogous treatment can be presented if $[OH^-] > 1$
- You need to understand this, but you will not be asked such cases on exams or quizzes.

- $C_A=1.00$
- The rules of proper sci notation require, since $[H^+][OH^-]=1.00 \times 10^{-14}$, that $C_B=1.00$, also
- Either both coefficients are 1.00 or neither is.
- In such a case, the results become trivial
- $O_A=E_A \quad O_B=E_B \quad O_A+O_B= E_A+E_B =14$
- $M_A=M_B=.00$
- What are pH, etc if $[OH^-]=0.0010$
- $pOH=3$
- $pH=11$
- $[H^+]=10^{-11}$
- You are responsible for cases of this type

What do we know so far?

- There are these things called acids and bases and a bunch of systems of definitions
- Substances can be classified as strong, neutral or weak according to their acid/base properties. Proper identification is a critical step in any analysis
- The autoionization of water is a major factor in determining $[H^+]$, $[OH^-]$, etc in water. K_w for water controlling the $[H^+]$ and $[OH^-]$ is an example of the LeChatelier Effect.
- In our analysis, emphasis is on proton transfer in aqueous media
- In fully describing an aqueous solution with regards to its acid/base characteristics there are seven quantities that should be given: $[H^+]$, $[OH^-]$, pH, pOH, $[HA]$ or $[B]$, $[A^-]$ or $[BH^+]$ and % ionization
- Analysis of solutions of strong and neutral species is very straightforward, while weak species require a more detailed treatment, made much easier by use of the weak acid approximation

Weak acid Approximation

- In general, weak acids ionize to such a small extent that $[H_3O^+] \ll C_i$
- The equilibrium expression simplifies to:
 - $K_a = [H_3O^+]^2 / C_i$
 - $[H_3O^+] = (K_a * C_i)^{1/2}$
 - The resultant $[H_3O^+]$ is considered valid if is less than 5% of C_i
- Why 5%? - Generally neither the K nor the C_i is known to more than two sig figure precision. The $[H_3O^+]$ obtained from the approximation is greater than the value gotten from the exact solution and the two will agree to two sig figures if $[H_3O^+] \approx < 0.05 * C_i$. See table below

C_i	K_a	Approx	Exact	5% of C_i	?
0.1	2.50E-06	5.00E-04	4.99E-04	0.005	valid
0.1	5E-06	7.07E-04	7.05E-04	0.005	valid
0.1	2.5E-05	1.58E-03	1.57E-03	0.005	valid
0.1	0.000125	3.54E-03	3.47E-03	0.005	valid
0.1	0.000625	7.91E-03	7.60E-03	0.005	invalid
0.1	0.003125	1.77E-02	1.62E-02	0.005	invalid
0.1	0.015625	3.95E-02	3.25E-02	0.005	invalid

- In general if $C_i > 40 * K_a(K_b)$ then the approx is valid

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

Sample “typical” exam question

- Provide complete acid base treatments of the following. If the species is neutral, simply write “pH=7”
- 0.026M HCl
- 1.25×10^{-2} M acetic acid
- .0067M potassium nitrate
- 4.5×10^{-4} M NH_3
- 0.65M NaHCO_2

What's the deal with conjugates?

- Conjugates of monoprotic strong acids are neutral
- If the species involved are weak
- $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+ \quad K_a$
- $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^- \quad K_b$
- Remembering the rules on combining equilibria (you do remember those, don't you), what is the value of K if you add the above two equations?
- $K_a * K_b$
- Chemically, what is the result of summing the two reactions?
- $2\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}_3\text{O}^+$
- What is the K for this?
- K_w
- Thus, for a conjugate acid/base pair $K_a * K_b = K_w$.
- Note: the rules relating $[\text{H}^+]$ and $[\text{OH}^-]$ also work for relating K_a and K_b
- Two major issues emerge from this
 - It is clear that K_a and K_b are inversely related. Thus, the stronger the acid, the weaker is its conjugate base and vice versa
 - The number of species for which Ks are known and the number of problems is doubled
- Strong acids typically have $K_a > 10^6$. Why are their conjugate bases neutral?
- Identify each of the following and calculate its K value: potassium cyanide, $\text{C}_6\text{H}_5\text{NH}_3^+$, CH_3CO_2^- , $\text{C}_5\text{H}_5\text{NH}^+$

Proton transfer in general

- For the reaction:
 - $\text{HA}(\text{aq}) + \text{B}(\text{aq}) \rightleftharpoons \text{A}^-(\text{aq}) + \text{HB}^+(\text{aq})$
- The following equil expression can be written
 - $K_{\text{rxn}} = [\text{A}^-][\text{HB}^+] / [\text{HA}][\text{B}]$
 - It should be clear that the value of the above K is of use in predicting the degree to which a proton transfer occurs
- The process can be viewed as occurring in the following series of steps (Hess' Law strikes again):
 - $\text{HA}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{A}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \quad K_a$
 - $\text{B}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad K_b$
 - $\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons 2\text{H}_2\text{O} \quad K = 1/K_w$
- Using the rules for combining equilibria, the overall K is $K_{\text{rxn}} = K_a * K_b / K_w$ (these are not the Ks for a conj pair)

- There are several important consequences of this:
- The K for any proton transfer reaction is calculable, provided the K_a and K_b for the acid and base are known
- The following statements are general “rules of thumb” for describing proton xfer rxns:
- Acid-base reactions run “downhill and to completion” with the final solution being dominated by the weaker acid and base pair
- The strongest acid or base that can exist in a given solvent are the conjugates of the solvent. All species stronger than that are converted to the conjugates. This is called the “leveling effect.”

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 is termed as “going 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

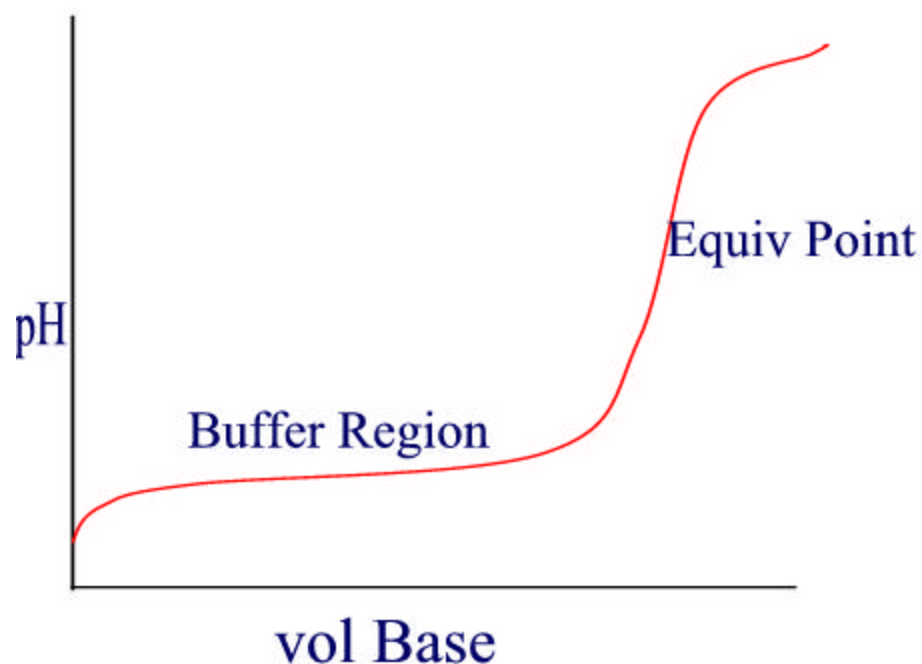
The titration of a 259mg sample of a weak acid requires 34.4mL of .100M NaOH. What is the equivalent weight of the acid?

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?

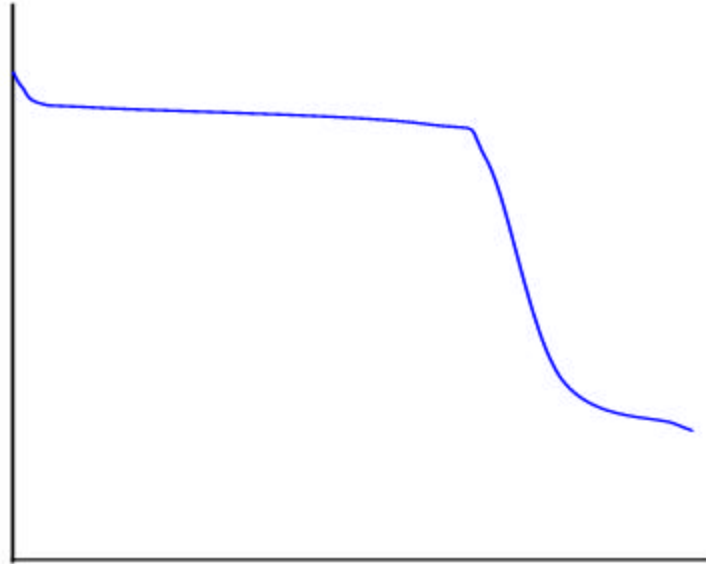
What volume in mL of .100M NaOH would be required to titrate a 0.574g sample of a weak acid with an equivalent weight of 190grams ?

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
 - 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 nearly the same. Ex: tartaric acid(table 15.6)

- 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 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.