CH14 - EQUATIONS

KEY EQUATIONS

• Rate $= -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$	[14.4]	Relating rates to the components of the balanced chemical equation $a\,A + b\,B \longrightarrow c\,C + d\,D$
• Rate $= k[A]^m[B]^n$	[14.7]	General form of a rate law for the reaction $A + B \longrightarrow$ products
• $\ln[A]_t - \ln[A]_0 = -kt$ or $\ln\frac{[A]_t}{[A]_0} = -kt$	[14.12]	The integrated form of a first-order rate law for the reaction $A \longrightarrow$ products
• $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	[14.14]	The integrated form of the second-order rate law for the reaction $A \longrightarrow$ products
• $t_{1/2} = \frac{0.693}{k}$	[14.15]	Relating the half-life and rate constant for a first-order reaction
• $k = Ae^{-E_a/RT}$	[14.19]	The Arrhenius equation, which expresses how the rate constant depends on temperature
• $\ln k = -\frac{E_a}{RT} + \ln A$	[14.20]	Linear form of the Arrhenius equation

ORDER

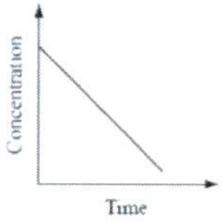
0 $[A]_t = -kt + [A]_0$ 56 57

1 $\ln[A]_t = -kt + \ln[A_0]$ 65 66

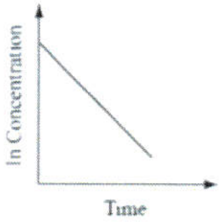
2 $\frac{1}{[A]_t} = -kt + \frac{1}{[A_0]}$

Kinetics:

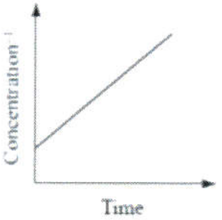
You are in search of linear data! Here comes the elegant part... If you do the set of graphs in this order with the *y*-axes being "**c**oncentration", "**n**atural log of concentration" and "**r**eciprocal concentration", the alphabetical order of the *y*-axis variable leads to 0, 1, 2 orders respectively for *that* reactant.



Zero order
k = negative slope



First order
k = negative slope



Second order
k = the slope

You can now easily solve for either time or concentration once you know the order of the reactant. Just remember $y = mx + b$. Choose the set of variables that gave you the best straight line (r value closest to ± 1) and insert them in place of x and y in the generalized equation for a straight line. "A" is reactant A and A_o is the initial concentration of reactant A at time zero [the *y*-intercept].

	y	$=$	mx	$+$	b
zero order	$[A]$	$=$	$-kt$	$+$	$[A_o]$
first order	$\ln[A]$	$=$	$-kt$	$+$	$\ln[A_o]$
second order	$1/[A]$	$=$	kt	$+$	$1/[A_o]$

Also recognize that $|\text{slope}| = k$, since the rate constant is NEVER negative. If you are asked to write the rate expression [or rate law] it is simply Rate = $k[A]^{\text{order you determined from analyzing the graphs}}$

Graphing Calculator Tutorial Set up your calculator so that *time* is always in L1. Use L2, L3 and L4 to display the *y*-variables. Remember the list for what is placed on the *y*-axis is alphabetical (concentration, natural log of concentration and reciprocal concentration).

L1 = time (*x*-variable throughout!)		
L2 = concentration	$[A]$	straight line infers zero order
L3 = ln concentration	$\ln[A]$	straight line infers first order
L4 = reciprocal concentration	$1/[A]$	straight line infers second order

Use this system to set up the data given in the following exercise:

We are going to perform 3 linear regressions to determine the order of the reactant. They will be L1,L2; L1,L3; L1,L4. Next, we will determine which regression has the best *r*-value [linear regression correlation coefficient in big people language!] We will also paste the best regression equation Y= so that we can easily do other calculations commonly required on AP Chemistry Exam problems.

Equilibrium

The significance of K:

$K > 1$ means that the reaction **favors the products** at equilibrium

$K < 1$ means that the reaction **favors the reactants** at equilibrium

THE EQUILIBRIUM EXPRESSION: A general description of the equilibrium condition proposed by Gudberg and Waage in 1864 is known as the Law of Mass Action. Equilibrium is temperature dependent, however, it does not change with concentration or pressure.

- **equilibrium constant expression**--for the general reaction

  $$aA + bB \rightleftarrows cC + dD$$

Equilibrium constant: $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ * Note* K, K_c, K_{eq} may all be used here!

The product concentrations appear in the numerator and the reactant concentrations in the denominator. ***Each** concentration is raised to the power of its stoichiometric coefficient in the balanced equation.*

- [ ] indicates concentration in Molarity (mol/L)
- K_c--is for concentration (aqueous)
- K_p--is for partial pressure (gases)
- "K" values are often written without units

- USING EQUILIBRIUM CONSTANT EXPRESSIONS
- **Pure solids**--do not appear in expression—you'll see this in K_{sp} problems soon!
- **Pure liquids**--do not appear in expression—$H_2O(l)$ is pure, so leave it out of the calculation
- **Water**--as a pure liquid or reactant, does not appear in the expression. (55.5 M will not change significantly)
  - Weak acid and weak base equations are heterogeneous [multi-states of matter; pure liquid and aqueous components] equilibria.

  - Solubility of salts also fits into this category. The initial solid component has a constant concentration and is therefore left out of the equilibrium expression.

- K_c & K_p--**NOT INTERCHANGEABLE!** $\boldsymbol{K_p = K_c(RT)^{\Delta n}}$
  where Δn is the change in the number of moles of gas going from reactants to products:

- Δn = total moles gas produced − total moles gas reacting
  - R = universal gas law constant 0.0821 L atm/ mol K
  - T = temperature in Kelvin

- $Kc = Kp$ **if** the number of moles of gaseous product = number of moles of gaseous reactant since $(RT)^{\Delta n} = (RT)^0 = 1$

- $K_p = K_c(RT)^{\Delta n}$ is often referred to as the "politically correct" (pc) equation to help you remember the order of the Ks in the equation!

THE REACTION QUOTIENT

For use when the system is NOT at equilibrium.
For the general reaction

$$aA + bB \rightleftarrows cC + dD$$

$$\text{Reaction quotient} = Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Q_c has the appearance of K but the concentrations are *not necessarily* at equilibrium.

1. **If $Q < K$, the system is not at equilibrium:** Reactants → products to make $Q = K$ at equil.
2. **If $Q = K$, the system is at equilibrium.**
3. **If $Q > K$, the system is not at equilibrium:** Reactants ← products to make $Q = K$ at equil.

Quite useful for predicting what will happen under special conditions.

SOME CALCULATIONS WITH THE EQUILIBRIUM CONSTANT

General steps for solving equilibrium problems.

1. Set up "**RICE**" **TABLE**—write a balanced **r**eaction, place **i**nitial **c**oncentrations into the table, determine the **c**hange in initial concentrations in terms of x, calculate the **e**quilibrium concentration expressions ($0.25\ M - x$).

   R = write a balanced reaction for the predominant reacting species
   I = fill in the initial concentrations
   C = determine the change that is taking in place in terms of x
   E = express the equilibrium concentrations in terms of x

2. Set up the equilibrium expression and set it equal to its value, if given.
3. Celebrate if you are given equilibrium concentrations! Just skip down to the "E" line and fill them in. You may be asked to work backwards to determine the "change" in equilibrium.
4. If you are given a K value, then use it to solve for x and use x to calculate the equilibrium concentrations.

Hints:

- Look for very small K values (where $K < 10^{-5}$), "x" may be negligible.
- If "x" is large enough to impact the equilibrium values, then you must subtract it from the initial concentration. Your math will be simplified if the problem is a perfect square. If not, you must use the quadratic formula. You are allowed to use your calculator with a solver or program for solving the quadratic.
- If none of the initial concentrations are zero, then Q must be calculated first to determine the direction of the shift before following the above general steps.

EXTERNAL FACTORS AFFECTING EQUILIBRIA

- **Le Chatelier's Principle:** If a stress is applied to a system at equilibrium, the position of the equilibrium will shift in the direction which reduces the stress.
- Shifts occur to reestablish equilibrium positions. Think about *K*! Generally, $\frac{[\text{products}]}{[\text{reactants}]}$
- Adding or removing a reagent causes the equilibrium to shift to reestablish *K*.
  As long as you milk a "mamma" cow, she keeps making more milk!
- Increasing pressure causes the equilibrium to shift to the side containing the fewest number of moles of gas. The converse is also true.
- Adding a catalyst to a reaction has causes no shift and has NO EFFECT on *K*. It just causes equilibrium to be established faster!
- Changing the temperature is a lot like adding or removing a "reactant or product". Well, as long as you think of *heat energy* as a "reactant" or "product".

Think of it this way:

ENDOTHERMIC: $A + B \rightleftarrows C + D$ $+\Delta H$ value (heat is added into the system $\therefore$ heat is a reactant)

Rewrite: $A + B + heat \rightleftarrows C + D$

EXOTHERMIC: $A + B \rightleftarrows C + D$ $-\Delta H$ value (heat is lost from the system $\therefore$ heat is a product)

Rewrite: $A + B \rightleftarrows C + D + heat$

Chemical Equilibrium

$K >> 1$ Favors Product

$K << 1$ Reactants

Endo ↑T = ↑K

Exo ↑T = ↓K

$\Delta H < 0$ Exo

$\Delta H > 0$ Endo

↓K = ↓Product ↑Reactant

↑K = ↑Product ↓Reactant

Pressure

↑Pressure = ↓ Side with most gas moles

↓Pressure = ↑ Side with Most gas moles

$$K = \frac{\text{Products}}{\text{Reactants}}$$

↑Reactants ⇌ ↑Products

↓Reactant ⇌ ↓Products

Never include Pure solid or liquid IN Equilibrium Equation.

$$PbCl_{2(s)} \rightleftharpoons Pb^{+2}_{(aq)} + 2Cl_{(aq)}$$

$$K_c = [Pb^{+2}][Cl^-]^2$$

Reaction Quotient = Q Starting Conc

Q = K Equilibrium

Q > K Product Too Large move To Reactants

Q < K Reactant Too Large move To Product

Ksp solubility

- For a saturated solution of AgCl, the equation would be:
  $$AgCl(s) \rightleftarrows Ag^{+}(aq) + Cl^{-}(aq)$$
- The solubility product expression for the AgCl(s) precipitate would be:
  $$K_{sp} = [Ag^{+}][Cl^{-}]$$
- The AgCl(s) does not appear in the equilibrium expression since solids are left out. Why? *Because*, the concentration of the solid remains relatively constant.

Example: Lead(II) chloride dissolves to a slight extent in water according to the equation below.

$$PbCl_2(s) \rightleftarrows Pb^{+2} + 2Cl^{-}$$

Calculate the K_{sp} if the lead ion concentration has been found to be $1.62 \times 10^{-2} M$.

If lead's concentration is x, then chloride's concentration is 2x. So. . . .

$$K_{sp} = (1.62 \times 10^{-2})(3.24 \times 10^{-2})^2 = 1.70 \times 10^{-5}$$

K_{sp} AND THE REACTION QUOTIENT, Q

With some knowledge of the reaction quotient, we can decide

- whether a precipitate (ppt) will form AND
- what concentrations of ions are required to begin the precipitation of an insoluble salt.

1. **$Q < K_{sp}$, the system is not at equil. (*un*saturated)**
2. **$Q = K_{sp}$, the system is at equil. (saturated)**
3. **$Q > K_{sp}$, the system is not at equil. (*supersaturated)***

Precipitates form when the solution is supersaturated!!!

Acid Base:

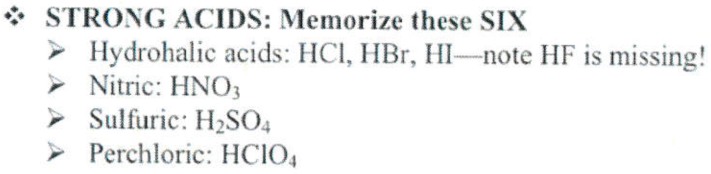
$K_w = K_a \times K_b$

$pH = -\log[H^+]$

$[H^+] = 10^{-pH}$

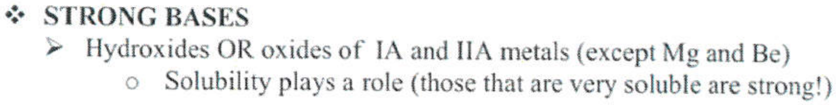
$14 = pH + pOH$

Strong acids completely disassociate

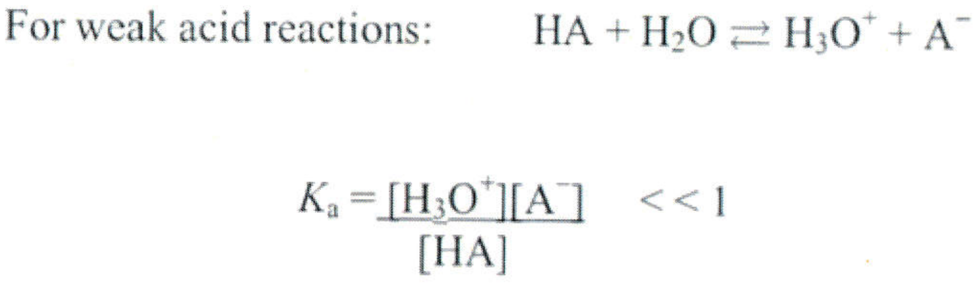


- **STRONG ACIDS: Memorize these SIX**
  - Hydrohalic acids: HCl, HBr, HI—note HF is missing!
  - Nitric: HNO_3
  - Sulfuric: H_2SO_4
  - Perchloric: $HClO_4$

Strong Bases



- STRONG BASES
  - Hydroxides OR oxides of IA and IIA metals (except Mg and Be)
    - Solubility plays a role (those that are very soluble are strong!)



For weak acid reactions: $HA + H_2O \rightleftarrows H_3O^+ + A^-$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad << 1$$

Calculate the pH of a 10.10 M solution of acetic acid. The K_a of acetic acid is 1.8×10^{-5}.

Reaction	$HC_2H_3O_2$	$\rightleftarrows$	H^+	$+\ C_2H_3O_2^-$
Initial	0.10		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$0.10-x$		x	x

$$K_a = \frac{\left[H^+\right]\left[C_2H_3O_2^-\right]}{HC_2H_3O_2} = 1.8\times10^{-5} = \frac{x^2}{0.10-x}$$

By cross multiplying and NOT neglecting x, you get $x^2 = 1.8 \times 10^{-6} - 1.8 \times 10^{-5}x$; collect like terms and use either the solver on your graphing calculator or a quadratic formula solving program you've loaded on your calculator (all of this to avoid arithmetic mistakes!) to solve for x. You should determine that $x = [H^+] = 0.0013327$ (way too many sig. figs, I know!)

and that the pH = − log (0.0013327) = 2.88 (2 SF)

Had we *"neglected x"*, the math simplifies to

$$K_a = \frac{\left[H^+\right]\left[C_2H_3O_2^-\right]}{HC_2H_3O_2} = 1.8\times10^{-5} = \frac{x^2}{0.10-\cancel{x}} \text{ and } x^2 = 1.8 \times 10^{-6}$$

So, take the square root of each side to get

$$\sqrt{x^2} = \sqrt{1.8 \times 10^{-6}}$$

$$x = 0.00134 = \left[H^+\right]$$

pH = − log (.001341) = 2.87 (2 SF) which is mighty, mighty close, so it is a really good approximation.

- **THE STRONGER THE ACID THE WEAKER ITS CB,** ***the converse is also true.***

The equilibrium expression for **bases** is known as the K_b.

for weak base reactions: $B + H_2O \rightleftarrows HB^+ + OH^-$

$$K_b = \frac{[HB^+][OH^-]}{[B]} \ll 1$$

- **Neutral Salts**--Salts that are formed from the cation of a strong base reacting with the anion of a strong acid are neutral. Beware of solubility issues! One salt such is $NaNO_3$. Think about which acid reacted with which base to form the salt…if both the acid and base are strong, then the salt is neutral.

- **Basic Salts**--Salts that are formed from the cation of a strong base reacting with the anion of a weak acid are basic. Again, beware of solubility issues! The anion hydrolyzes the water molecule to produce hydroxide ions and thus a basic solution. $K_2C_2H_3O_2$ should be basic since $C_2H_3O_2^-$ is the CB of the weak acid $HC_2H_3O_2$' while K^+ does not hydrolyze appreciably.

$$C_2H_3O_2^- + H_2O \rightleftarrows \underset{\text{strong base}}{OH^-} + \underset{\text{weak acid}}{HC_2H_3O_2}$$

- **Acidic Salts**- Salts that are formed from the cation of a weak base reacting with the anion of a strong acid are acidic. The cation hydrolyzes the water molecule to produce hydronium ions and thus an acidic solution. NH_4Cl should be weakly acidic, since NH_4^+ hydrolyzes to give an acidic solution, while Cl^- does not hydrolyze.

$$NH_4^+ + H_2O \rightleftarrows \underset{\text{strong acid}}{H_3O^+} + \underset{\text{weak base}}{NH_3}$$

  - If both the cation and the anion contribute to the pH situation, compare K_a to K_b.
  - If K_b is larger, basic! The converse is also true.

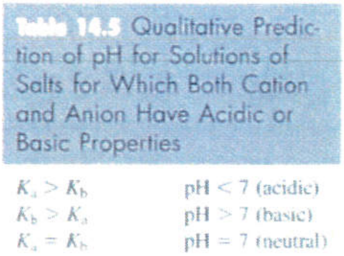


Table 14.5 Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties

$K_a > K_b$	pH < 7 (acidic)
$K_b > K_a$	pH > 7 (basic)
$K_a = K_b$	pH = 7 (neutral)

Buffers

EQUILIBRIUM

$$HF + H_2O \rightleftharpoons H^+ + F^-$$

$HCl \rightarrow H^+ + Cl^-$

ADD ACID

$$HF + H_2O \rightleftharpoons \uparrow H^+ + F^-$$

ADD BASE

$$HF + H_2O \rightleftharpoons \downarrow H^+ + F^-$$

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

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$pH = pK_a + \log \frac{[Base]}{[Acid]}$$

Henderson–Hasselbalch Equation

What is the pH of a buffer that is 0.12 *M* in lactic acid, $CH_3CH(OH)COOH$, and 0.10 *M* in sodium lactate? K_a for lactic acid is 1.4×10^{-4}.

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Henderson–Hasselbalch Equation

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

$$pH = -\log(1.4 \times 10^{-4}) + \log\frac{(0.10)}{(0.12)}$$

$$pH = 3.85 + (-0.08)$$

$$pH = 3.77$$

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Buffers

There are a few background concepts/skills at which students need to be proficient before any method of solving buffer problems becomes effective:

- Students must know the conjugate A/B concept to be successful at buffer problems. This means they understand that HA has A^- as it's conjugate and that NaA is not only the salt, but that any soluble salt releases the conjugate
- $pH = -\log[H^+]$
- $K_a \times K_b = K_w$
- Realize that any titration involving a weak A/B is a buffer problem. If I titrate HA with NaOH, then as soon as the first drop splashes into the container, I've made NaA^- which promptly dissociates into A^-

I use one and only one formula to solve buffer problems, this lessens student [and in my case, teacher] confusion! Here it is:

$$\left[H^+\right] = K_a \frac{\left[\text{Acid}\right]}{\left[\text{Base}\right]}$$

ACID-BASE TITRATION CURVES

Only when the acid AND base are both strong is the pH at the equivalence point 7. Any other conditions and you get to do a nasty equilibrium problem. It's really a stoichiometry problem with a limiting reactant. The "excess" is responsible for the pH

Weak acid + strong base ☞ eq. pt. $> pH\ 7$

Strong acid + weak base ☞ eq. pt. $< pH\ 7$

There is a distinction between the equivalence point and the end point. The end point is when the indicator changes color. If you've made a careful choice, the equivalence point, when the number of moles of acid = number of moles of base, will be achieved at the same time.

FIVE POINTS OF INTEREST ALONG A TITRATION CURVE for weak acids/bases:

1. The pH before the titration begins. Treat as usual, the acid or base in the flask determines the pH. If weak, a RICE table is in order.

2. The pH on the way to the equivalence point. You are in the "land of buffer" as soon as the first drop from the buret makes a splash and reacts to form the salt. Whatever is in the burette is the "added" part. Use $\left[\mathrm{H}^{+}\right]=K_a\frac{[\mathrm{Acid}]}{[\mathrm{Base}]}$ to solve for the hydrogen ion concentration and subsequently the pH. Either the acid or the base [whichever is in the burette] starts at ZERO.

3. The pH at the midpoint of the titration (½ equivalence point): $\left[\mathrm{H}^{+}\right]=K_a\frac{[\mathrm{Acid}]}{[\mathrm{Base}]}$ on the way *to* the equivalence point as explained above; once the midpoint is reached, $[\mathrm{H}^+] = K_a$ since ½ of the acid or base has been neutralized, AND the resulting solution in the beaker is composed of the half that remains AND the salt. That means the A/B term is a big tall ONE so, it follows that $\mathrm{pH} = \mathrm{p}K_a$

4. The pH *at* the equivalence point.—you are simply calculating the pH of the *salt*, all the acid or base is now neutralized [to salt + water!]. Write the hydrolysis reaction as the "R" of your RICE table. [Examples follow the fifth point of interest…]

5. The pH beyond the equivalence point—it's stoichiometry again with a limiting reactant. Calculate the *molarity* of the EXCESS and solve for either pH directly (excess H^+) or pOH (excess OH^-) and subtract it from 14 to arrive at pH. Be sure to track the total volume when calculating the *molarity*!

LEARNING TO WRITE SALT HYDROLYSIS REACTIONS

Recall that when quantities of acid and base react, a neutralization reaction takes place and the products of such a reaction are salt and water. The trouble is that not all salts are neutral. However, reasoning through the pH of a salt is *easy* as is writing the subsequent hydrolysis reaction. Ponder the following points:

- "Hydrolysis" translates into "water splitting" but the salt is also split. The rest of this will be much easier if you think of H_2O as HOH and as a reactant. Essentially, a hydrolysis reaction is the reverse of a neutralization reaction and is written in net ionic form for all *soluble* salts.
- IF a strong base is reacted with a weak acid, "Strong wins!" and the salt is basic, thus OH^- forms as a product.
- IF a strong acid is reacted with a weak base, "Strong wins!" and the salt is acidic, thus H^+ forms as a product.
- The "Strong" portion of the acid or base is source of the "Spectator" ion.
- The remaining ion (or neutral molecule) is the reactant that reacts with the water.

Start the same way every time you try to write a hydrolysis reaction…draw the arrow in the center of your answer space!

$$\rightarrow$$

It's a hydrolysis reaction, water is a reactant and splits into H^+ and OH^-, so write it as HOH until you get the hang of this process. Your reaction looks like this so far:

$$+ \quad HOH \rightarrow$$

Recap what you now know: NaCN is a basic salt. Since it is basic, OH^- is a product. Your reaction improves…

$$+ \quad HOH \rightarrow OH^-$$

More knowledge: Na^+ is a spectator (since "Strong, Spectator"—it's an alliteration, get it? Strong and Spectator both start with an "S".) leaving CN^- as the other reactant. Your reaction improves yet again…

$$CN^- + HOH \rightarrow OH^-$$

Now, think…think…think. IF HOH released OH^- as a product, then H^+ is left to react with the negative cyanide ion. Your final improvement to the reaction finishes it off…

$$CN^- + HOH \rightarrow OH^- + HCN$$

Why is this such a big deal? A hydrolysis reaction is what you must plop into your RICE table to solve for the pH (or pOH) of an acid-base titration where *either* participant is weak. BECAUSE, at the equivalence point *moles acid = moles base = moles salt formed*. Just be sure and calculate the molarity of the salt by tracking the total volume before putting its concentration into the rice table.

Example 2 Write the hydrolysis reactions for the following salts:

a) KNO_2
b) NH_4NO_3
c) CH_3NH_3Cl
d) $NaClO_2$

a) Basic salt $NO_2^- + HOH \rightarrow OH^- + HNO_2$

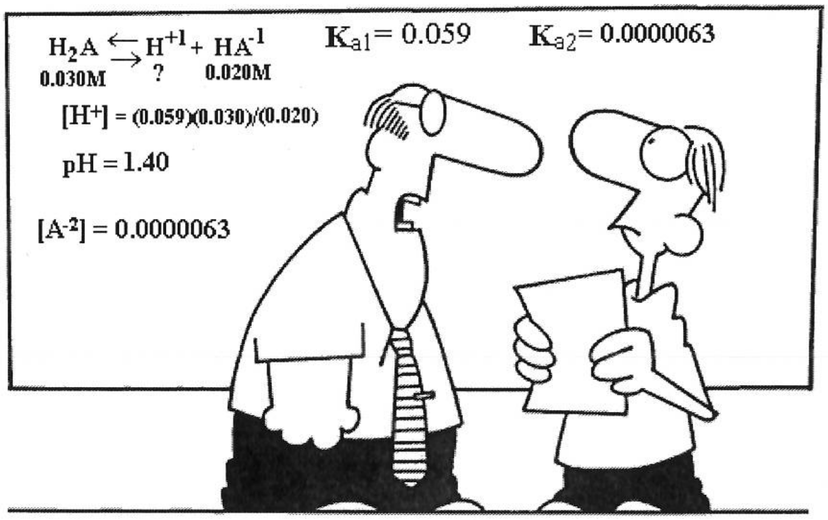
b) Acidic salt $NH_4^+ + HOH \rightarrow H^+ + NH_4OH$

c) Acidic salt $CH_3NH_3^+ + HOH \rightarrow H^+ + CH_3NH_3OH$

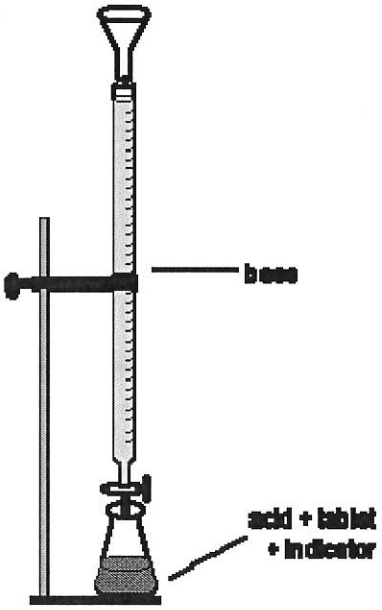
e) Basic salt $ClO_2^- + HOH \rightarrow OH^- + HClO_2$

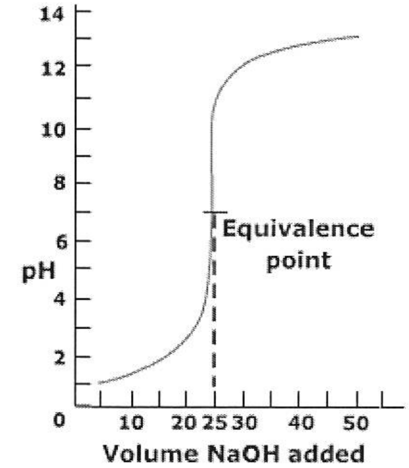
AP* Chemistry
Demystifying Titration Curves

This handout is meant to accompany the instructional video found at either http://www.vimeo.com/19007364 or http://www.edutube.org/en/video/ap-chemistry-interpreting-titration-curves. This won't make a lick of sense unless you watch the video containing the explanations!

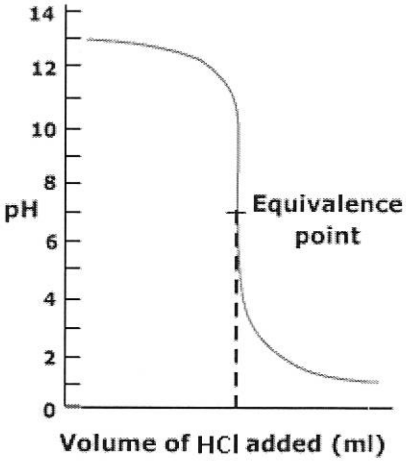


Why? Because I had to learn this stuff and now it's your turn!





Titration curve of strong acid (HCl) with a strong base (NaOH)



Titration curve of strong base (NaOH) with strong acid (HCl)

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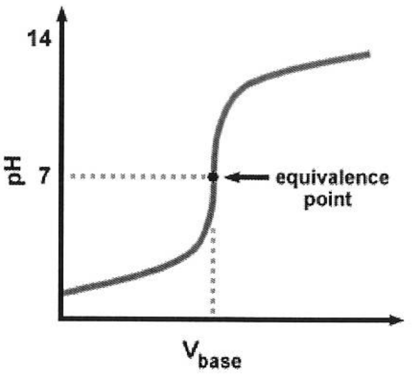
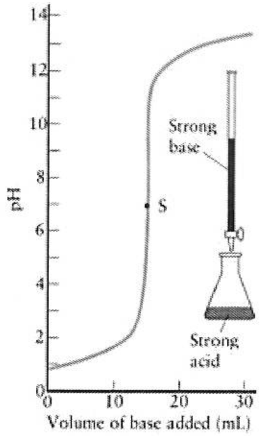
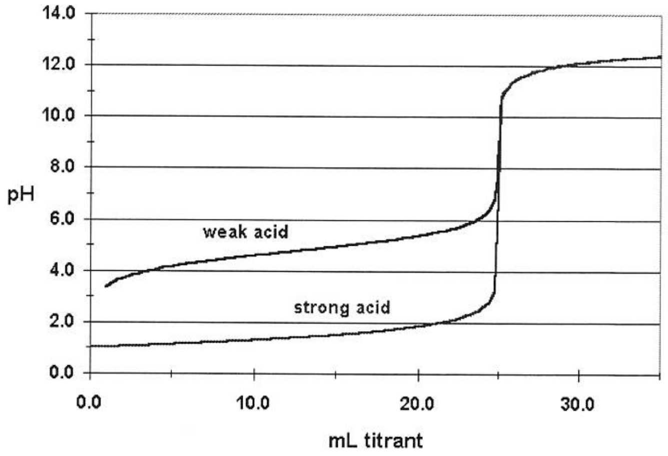
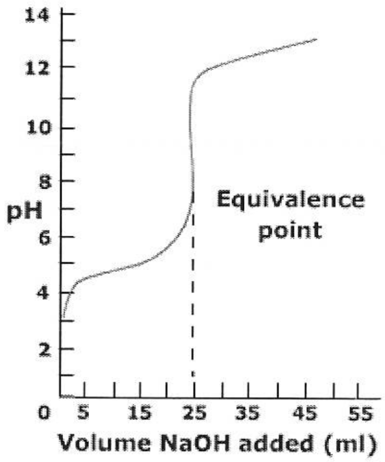
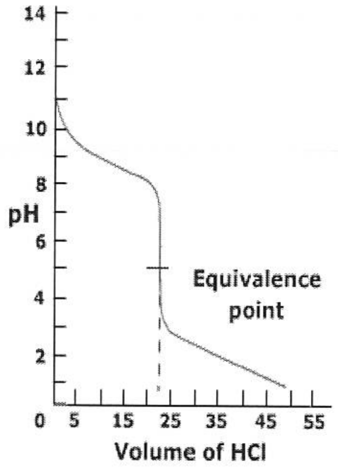




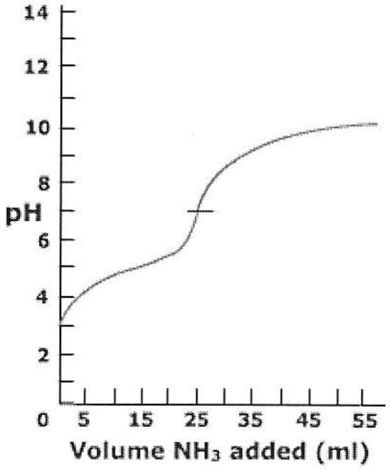




The pH titration curve of weak acid (CH_3COOH) and strong base (NaOH)



The pH titration curve of weak base(NH_4OH) and strong acid (HCl)



Titration curve of weak base (NH_4OH) and weak acid (CH_3COOH)

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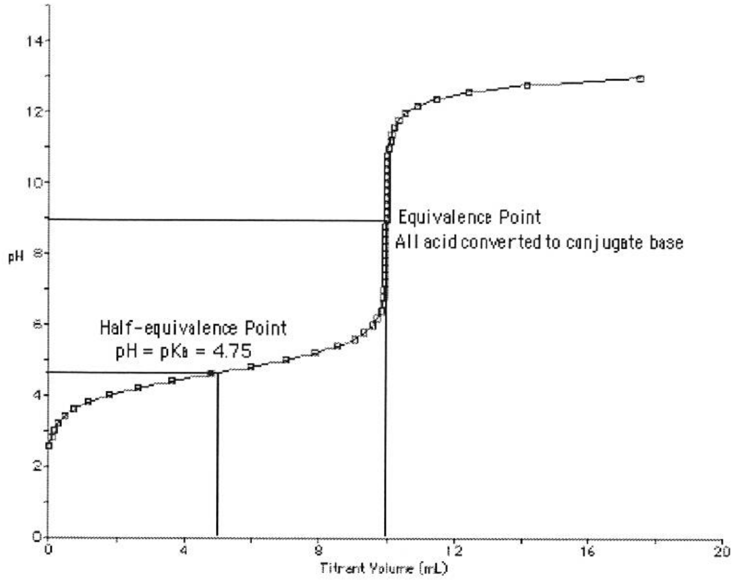
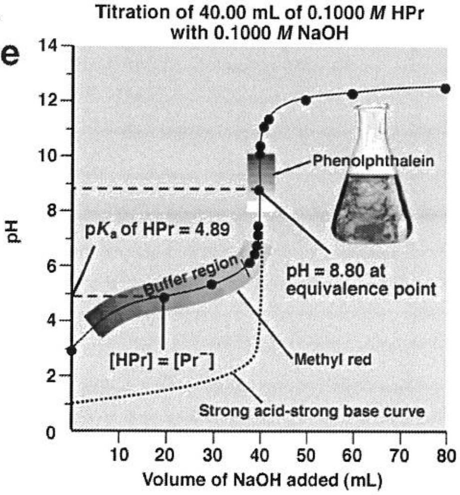
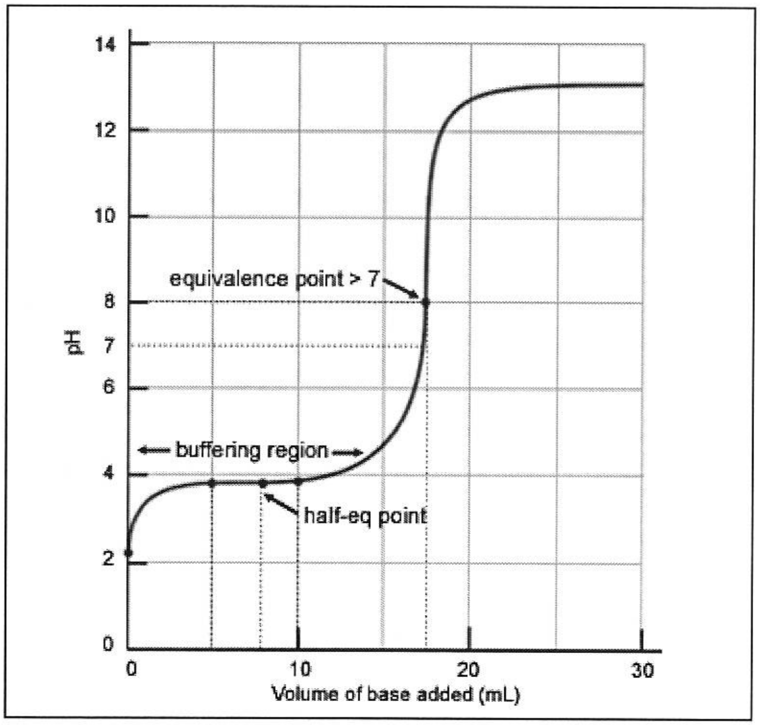


Weak Acid-Strong Base Titration Curve





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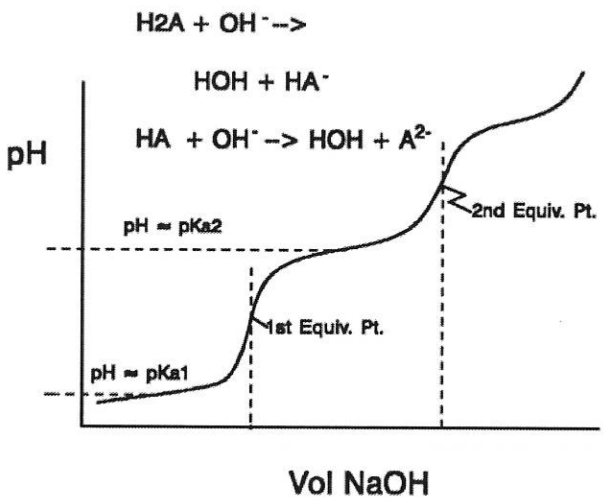

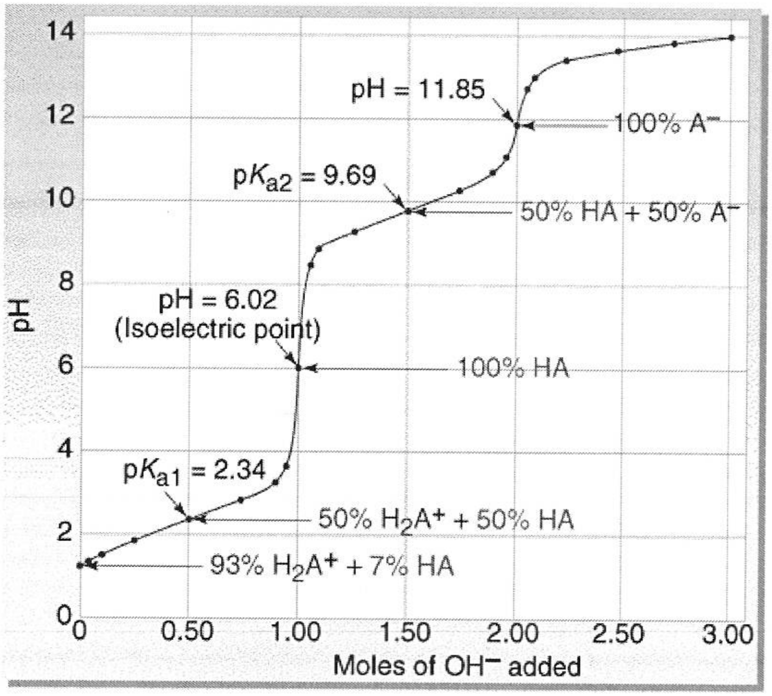

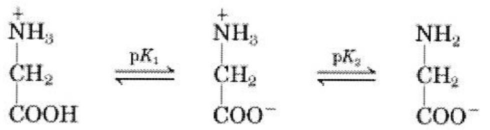

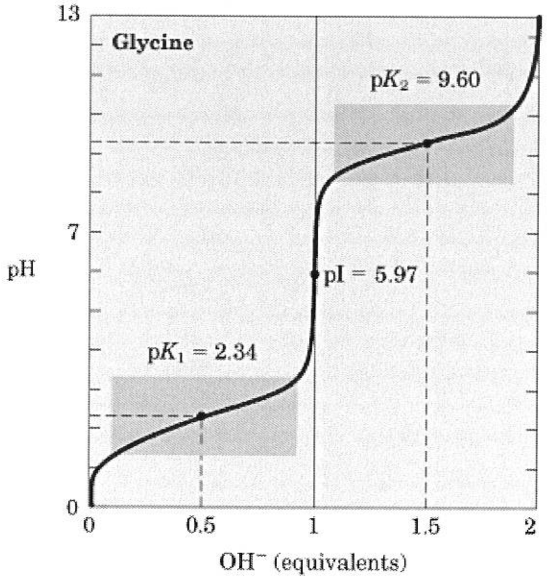

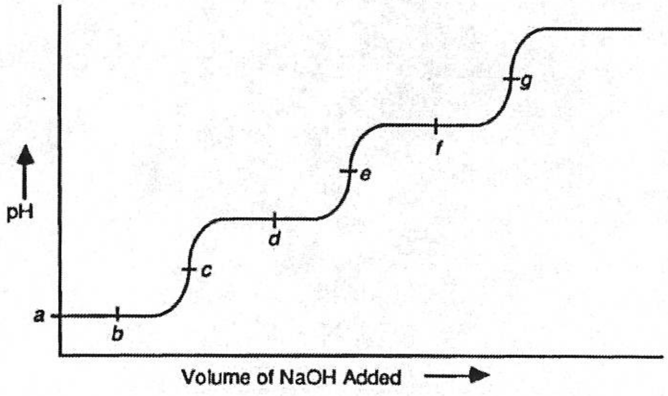

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