Dr. Zellmer
Time: 7 PM Sun.
40 min

Chemistry 1220
Spring Semester 2023
Quiz VIII

All Sections
March 26, 2023

Name ______ KEY ______ Rec. Instr. ______________________

1. A 25.0 mL of 0.020 M HCl is titrated with 0.010 M NaOH. What is the pH of the solution when 25.0 mL of NaOH has been added?

This is a strong acid, strong base titration (titrating the HCl with the NaOH). While it may not look like it is a stoichiometry problem to find which is in excess and then determine the pH.

For a titration question you should ALWAYS find the eq. pt. before you do anything else. Knowing where the eq. pt. is (volume of titrant needed to reach eq. pt.) can really help answer many questions.

Remember, **at the eq. pt.**: **moles H^+ = moles OH^-**

This is often stated as moles acid = moles of base
(but the statement above this is a more accurate statement)

a) How many mL of NaOH are required to reach the equivalence point?

The easiest way to do this, keeping the above in mind, is use the following eqn.:

$$M_a * V_a = M_b * V_b$$

Technically to get moles V would be in liters.
However, using this eqn. the volumes can be in mL.

$$V_b = \frac{M_a * V_a}{M_b} = \frac{(0.020\text{ M})\ (25.0\text{ mL})}{(0.0100\text{ M})} = \mathbf{50.0\ mL\ NaOH}$$

Want the pH at the point when 25.0 mL o f NaOH have been added. While this is halfway to the eq. pt. it's not the same as when a weak acid is titrated by a strong base (i.e. can't simply say pH = pK_a). However, this does tell us the limiting reactant will be the NaOH.

Two ways to approach this problem.

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1. (Cont.)

1) 1st way: Do stoichiometry problem to find excess moles of HCl and then find conc. of H^+.

<u>Stoich</u><u>. calc. - in</u> **<u>moles</u>**

$HCl + NaOH \longrightarrow Na^+ + Cl^- + H_2O$

It's a 1:1 ratio of HCl to NaOH.

Can use the net ionic eqn. $H^+ + OH^- \longrightarrow H_2O$

$$? \text{ mol NaOH} = 0.0250 \text{ L} \times \frac{0.010 \text{ mol NaOH}}{1 \text{ L}} = 0.00025 \text{ mol NaOH}$$

$$? \text{ mol HCl} = 0.0250 \text{ L} \times \frac{0.020 \text{ mol HCl}}{1 \text{ L}} = 0.00050 \text{ mol HCl}$$

	H^+	+	OH^-	$\longrightarrow$	H_2O	
initial	0.00050		0.00025		0	(all these are **moles**)
change	- 0.00025		- 0.00025		+ 0.00025	
comp.	0.00025		0		0.00025	

0.000250 moles of H^+ (HCl) in excess in a total volume of 50.0 mL.

$$[H^+] = [HCl] = \frac{0.00025 \text{ mol}}{0.0500 \text{ L}} = 5.\underline{\mathbf{0}} \times 10^{-3} \text{ M}$$

$$pH = -\log(5.\underline{\mathbf{0}} \times 10^{-3}) = 2.\underline{\mathbf{30}}$$

2) 2nd way: Find which is in excess by treating as a titration and using $M_a*V_a = M_b*V_b$.

Want the pH at the point when 25.0 mL o f NaOH have been added. While this is halfway to the eq. pt. it's not the same as when a weak acid is titrated by a strong base (i.e. can't simply say $pH = pK_a$). However, this does tell us the limiting reactant will be the NaOH and half of the HCl will have reacted leaving half of it. Can then determine the conc. of the excess HCl.

Half the moles of HCl will remain un-reacted since it's halfway to the eq. pt.

$$[HCl]_{excess} = \frac{\tfrac{1}{2}\text{ (original moles of HCl)}}{V_{total}}$$

$$[HCl]_{excess} = \frac{\tfrac{1}{2}(M_a * V_a)}{V_{a,\ orig} + V_{b,\ added}}$$

$$[HCl]_{excess} = \frac{\tfrac{1}{2}(0.020 \text{ M}) * (25.0 \text{ mL})}{(25.0 \text{ mL} + 25.0 \text{ mL})} = 5.\underline{\mathbf{0}} \times 10^{-3} \text{ M}$$

This is the same conc. of HCl as calculated above so you get the same pH. However, this is a much easier way to determine the [HCl] and pH.

2. A 25.00 mL sample of 0.100 M HCl is titrated with 0.100 M NaOH. What is the **pH** of the solution at the points where 24.9 and 25.1 mL of NaOH have been added.

NOT on quiz, just for practice.

This is an strong acid, strong base stoichiometry problem to find which is in excess and then determine the pH. While it may not look like it is the same as titration (a strong acid - strong base titration).

For a titration question you should ALWAYS find the eq. pt. before you do anything else. Knowing where the eq. pt. is (volume of titrant needed to reach eq. pt.) can really help answer many questions.

Remember, **at the eq. pt.**: **moles H^+ = moles OH^-**

This is often stated as moles acid = moles of base
(but the above is a more accurate statement)

a) How many mL of NaOH are required to reach the equivalence point?

The easiest way to do this, keeping the above in mind, is use the following eqn.:

$$M_a * V_a = M_b * V_b$$

Technically to get moles V would be in liters.
However, using this eqn. the volumes can be in mL.

$$V_b = \frac{M_a * V_a}{M_b} = \frac{(0.100\text{ M})(25.0\text{ mL})}{(0.100\text{ M})} = \mathbf{25.0\text{ mL NaOH}}$$

Want the pH at the point when 24.9 and 25.1 mL of NaOH have been added. This is just before and after the eq. pt. (where the pH would be 7.00). However, this does tell us the limiting reactant will be the NaOH when 24.9 mL of NaOH have been added (excess HCl) and the HCl will be the limiting reactant when 25.1 mL of NaOH have been added (excess NaOH).

Two ways to approach this problem.

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2. (Cont.)

1) 24.9 mL of NaOH:

a) First way: Do stoichiometry problem to find excess moles of HCl and then find conc. of H^+.

<u>**Stoich**. calc. - in **moles**</u>

$HCl + NaOH \longrightarrow Na^+ + Cl^- + H_2O$

It’s a 1:1 ratio of HCl to NaOH.

Can use the net ionic eqn. $H^+ + OH^- \longrightarrow H_2O$

$$? \text{ mol NaOH} = 0.0249 \text{ L} \times \frac{0.100 \text{ mol NaOH}}{1 \text{ L}} = 0.00249 \text{ mol NaOH}$$

$$? \text{ mol HCl} = 0.0250 \text{ L} \times \frac{0.100 \text{ mol HCl}}{1 \text{ L}} = 0.00250 \text{ mol HCl}$$

<u>Can use BCA or ICC table</u>

	H^+	+	OH^-	$\longrightarrow$	H_2O	
initial	0.00250		0.00249		0	(all these are **moles**)
change	- 0.00249		- 0.00249		+ 0.00249	
comp.	0.00001		0		0.00249	

0.00001 moles of H^+ (HCl) in excess in a total volume of 49.9 mL.

$$[H^+] = [HCl] = \frac{0.00001 \text{ mol}}{0.0499 \text{ L}} = 2.0\underline{\mathbf{0}} \times 10^{-4} \text{ M}$$

$$pH = -\log(2.0\underline{\mathbf{0}} \times 10^{-4}) = 3.\underline{\mathbf{70}}$$

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2. (Cont.)

b) 2nd way:

Find which is in excess by using $M_a{*}V_a = M_b{*}V_b$.

This was done above and it was found the HCl was in excess. Calculate the conc. of the excess HCl. There's 0.1 mL of excess HCl. This is just a dilution problem for the excess HCl.

$$[H^+]_{excess} = \frac{(\text{moles of excess } H^+)}{V_{total}}$$

$$[H^+]_{excess} = \frac{(M_a * V_{a,\ excess})}{V_{a,\ orig} + V_{b,\ added}}$$

$$[H^+]_{excess} = \frac{(0.100\text{ M}) * (0.1\text{ mL})}{(25.0\text{ mL} + 24.9\text{ mL})} = 2.0\underline{\mathbf{0}} \times 10^{-4}\text{ M} \qquad \text{(same as above)}$$

This is the same conc. of H^+ as calculated above so you get the same pH. However, this is a much easier way to determine the $[H^+]$ and pH.

2) 25.1 mL of NaOH:

a) First way: Do stoichiometry problem to find excess moles of NaOH and then find conc. of OH^-.

<u>**Stoich**. calc. - in **moles**</u>

$$? \text{ mol NaOH} = 0.0251\text{ L} \times \frac{0.100\text{ mol NaOH}}{1\text{ L}} = 0.00251\text{ mol NaOH}$$

$$? \text{ mol HCl} = 0.0250\text{ L} \times \frac{0.100\text{ mol HCl}}{1\text{ L}} = 0.00250\text{ mol HCl}$$

<u>Can use BCA or ICC table</u>

	H^+	+	OH^-	→	H_2O	
initial	0.00250		0.00251		0	(all these are **moles**)
change	- 0.00250		- 0.00250		+ 0.00250	
comp.	0		0.00001		0.00250	

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2. (Cont.)

0.00001 moles of OH^- (NaOH) in excess in a total volume of 50.1 mL.

$$[OH^-] = [NaOH] = \frac{0.00001 \text{ mol}}{0.0501 \text{ L}} = 1.9\underline{\mathbf{9}}6 \times 10^{-4} \text{ M}$$

$$pOH = -\log(1.9\underline{\mathbf{9}}6 \times 10^{-4}) = 3.\underline{\mathbf{70}}$$

$$pH = 14.00 - 3.70 = 10.\underline{\mathbf{30}}$$

b) 2nd way:

Find which is in excess by using $M_a * V_a = M_b * V_b$.

This was done above and it was found the NaOH was in excess. Calculate the conc. of the excess NaOH. There's 0.1 mL of excess NaOH. This is just a dilution problem for the excess NaOH.

$$[OH^-]_{excess} = \frac{(\text{moles of excess } OH^-)}{V_{total}}$$

$$[OH^-]_{excess} = \frac{(M_b * V_{b,\ excess})}{V_{a,\ orig} + V_{b,\ added}}$$

$$[OH^-]_{excess} = \frac{(0.100 \text{ M}) * (0.1 \text{ mL})}{(25.0 \text{ mL} + 25.1 \text{ mL})} = 1.9\underline{\mathbf{9}}6 \times 10^{-4} \text{ M} \qquad \text{(same as above)}$$

This is the same conc. of OH^- as calculated above so you get the same pOH and pH. However, this is a much easier way to determine the $[OH^-]$, pOH and pH.

Just for general information:

$$\text{Molarity} = \frac{\text{mol}}{\text{L}} = \frac{\text{mmol}}{\text{mL}} \qquad \text{where mmol is millimoles}$$

3. You have a solution of KOH of unknown concentration. A 15.00 mL sample of the KOH solution was titrated with 0.1050 M HNO_3. It took 21.35 mL of HNO_3 to reach the equivalence point. What was the concentration of the original KOH solution?

Want concentration of a base, KOH, in a sample. Using a titration with strong acid to determine the conc. of the KOH.

Remember, **at the eq. pt.**: **moles H^+ = moles OH^-**

This is often stated as **moles acid** = **moles of base**
(but the above is a more accurate statement)

In this case, since you are titrating KOH, a strong base HNO_3. The reaction is:

$$KOH + HNO_3 \longrightarrow HNO_3 + H_2O$$

The net ionic eqn is:

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

at the eq. pt. you have the following:

$$\text{moles of KOH} = \text{moles of } HNO_3$$

a) Determine the moles of HNO_3 required to get to the eq. pt. ($M*V_L$)

$$? \text{ mol } HNO_3 = 0.02135 \text{ L } HNO_3 \times \frac{0.1050 \text{ mol } HNO_3}{\text{L soln}} = 2.24\underline{1}7 \times 10^{-3} \text{ mol } HNO_3$$

$$? \text{ moles of KOH} = 2.24\underline{1}7 \times 10^{-3} \text{ mol } HNO_3 \times \frac{1 \text{ mol KOH}}{1 \text{ mol } HNO_3} = 2.24\underline{1}7 \times 10^{-3} \text{ mol KOH}$$

You want the conc. of the ORIGINAL KOH solution, BEFORE you titrated the sample. You divide the moles of KOH by the volume of the sample (not the total volume after titration).

$[KOH] = (2.24\underline{1}7 \times 10^{-3} \text{ mol}) / (0.01500 \text{ L}) = 0.149\underline{4}5 \text{ M} = \mathbf{0.1495} \text{ M}$

b) The easier way to do this, keeping the above in mind, is use the following eqn.:

$$M_a * V_a = M_b * V_b$$

Technically to get moles V would be in liters.

However, using this eqn. the volumes can be in mL.

$$M_b = \frac{M_a * V_a}{V_b} = \frac{(0.1050 \text{ M})(21.35 \text{ mL})}{(15.00 \text{ mL})} = \mathbf{0.1495 \text{ M}}$$

Technically the M_a is the molarity of the H^+ and the M_b is the molarity of OH^-.

4. A 1.40 g sample of Vitamin C is dissolved in 100.0 mL of water and titrated with 0.250 M NaOH to the methyl orange equivalence point. The volume of the base used is 34.1 mL. What is the **molecular weight** of Vitamin C assuming one dissociable proton per molecule?

NOT on quiz, just for practice.

Want MW of an acid by doing a titration. Think **MOLAR MASS**.

$$M = \frac{\text{g}}{\text{mol}} = \frac{1.40\text{ g}}{?\text{ mol}}$$ Have mass, need moles

Need to write eqn. for the neutralization rxn.

States Vitamin C has one dissociable proton - monoprotic

Represent as HC

$$\text{HC} + \text{NaOH} \longrightarrow \text{Na}^+ + \text{C}^- + \text{H}_2\text{O}$$

It’s a 1:1 ratio of HC to NaOH.

So if we can find moles of NaOH required to neutralize the HC that’s also the moles of HC.

The 100.0 mL of H_2O is immaterial - amount of H_2O used doesn’t change the moles of HC present.

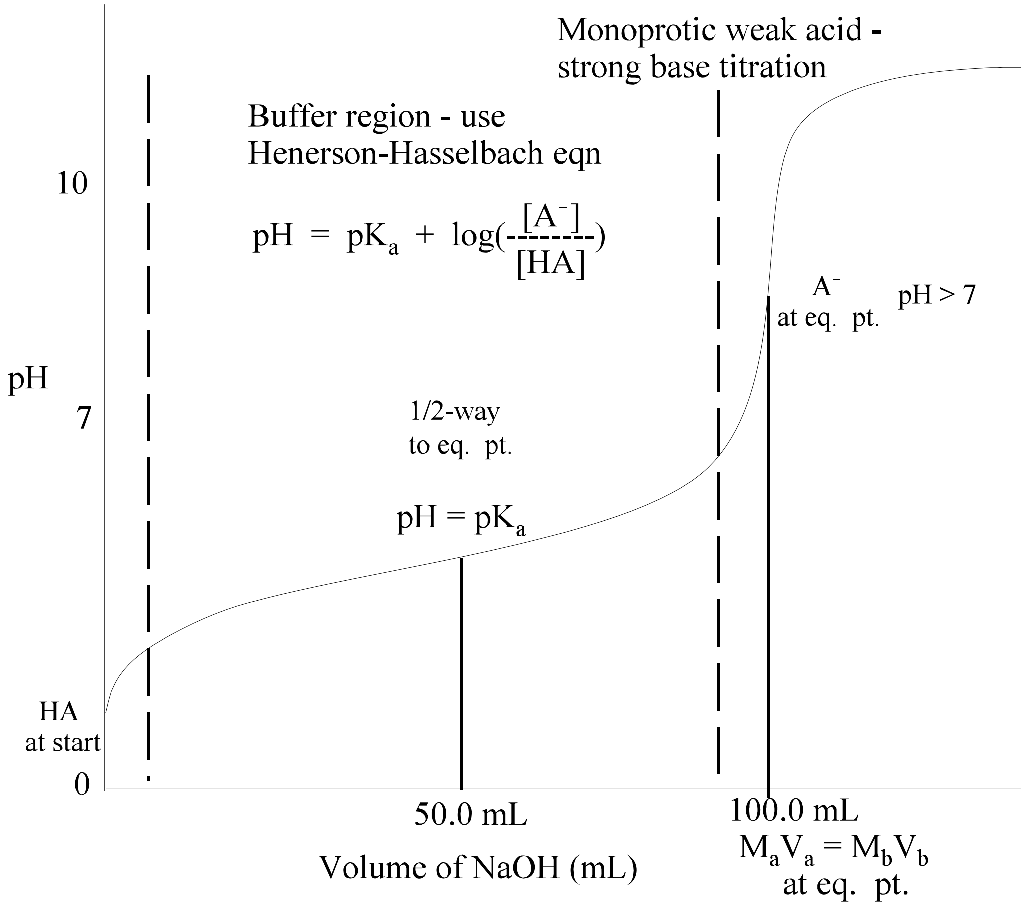
The “methyl orange” eq. pt. is immaterial. We don’t care about the indicator, only that it’s at eq. pt. (all HC has reacted at eq. pt.)

$$?\text{ mol NaOH} = 0.0341\text{ L} \times \frac{0.250\text{ mol NaOH}}{1\text{ L}} = 0.0085\underline{2}5\text{ mol NaOH}$$

$$?\text{ mol HC} = 0.0085\underline{2}5\text{ mol NaOH} \times \frac{1\text{ mol HC}}{1\text{ mol NaOH}} = 0.0085\underline{2}5\text{ mol HC}$$

$$M = \frac{1.40\text{ g HC}}{0.0085\underline{2}5\text{ mol HC}} = 16\underline{4}.22\text{ g/mol} = \mathbf{164}\text{ g/mol (164 amu)}$$

5. (12 pts) Answer the following questions for the titration of 40.0 mL of 0.100 M HCN with 0.0400 M NaOH. (HCN: $K_a = 4.9 \times 10^{-10}$) (**Show all work or explain**, including ICE tables, assumptions & check for % error when necessary.)



M_aV_a refers to the weak acid & M_bV_b refers to the NaOH titrant

For the sake of generality I used HA to stand for the weak acid. What you see below should apply to any monoprotic weak acid - strong base titration.

$HA + NaOH \longrightarrow Na^+ + A^- + H_2O$

net ionic eqn.: $HA + OH^- \longrightarrow A^- + H_2O$

For a titration question you should ALWAYS find the eq. pt. before you do anything else. Knowing where the eq. pt. is (volume of titrant needed to reach eq. pt.) can really help answer many questions.

Remember, **at the eq. pt.**: **moles H^+ = moles OH^-**

This is often stated as moles acid = moles of base

which is true for a monoprotic acid or monobasic base (1 OH^- in the formula) but **moles H^+ = moles OH^-** is a more general statement.

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5. (cont.)

a) (2 pts) How many mL of NaOH are required to reach the **equivalence point**?

Remember, at the eq. pt.: moles H^+ = moles OH^- (this is often stated as moles acid = moles of base but what I have is a more accurate statement)

This can be done in two ways.

1) determine the moles of acid, HCN, originally present and use the balanced eqn for the reaction of NaOH with the acid. (This is a stoichiometry problem as done in Chem 1210.)

$$HCN + NaOH \longrightarrow Na^+ + CN^- + H_2O$$

(Net Ionic Eqn.: $HCN + OH^- \longrightarrow CN^- + H_2O$)

This shows the reaction is 1:1, 1 mole of acid reacts with 1 mole of base.

$$? \text{ mL NaOH} = 0.0400 \text{ L HCN soln} \times \frac{0.100 \text{ mol HCN}}{1 \text{ L HCN soln}} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HCN}} \times \frac{1 \text{ L NaOH soln}}{0.0400 \text{ mol NaOH}} \times \frac{10^3 \text{ mL}}{1 \text{ L}}$$

= **100.0 mL NaOH**

2) easier way:

moles H^+ = moles OH^-

moles acid = moles base

$M_a * V_a = M_b * V_b$ (Technically molarity of H^+ and molarity of OH^-.)

M_a & V_a correspond to the weak acid being titrated
M_b & V_b correspond to the NaOH used for the titration (the titrant)

For a weak base being titrated by a strong acid this would be flipped (Mb and Vb would correspond to the weak base being titrated and Ma and Va would correspond to the strong acid, the titrant).

Technically to get moles V would be in liters.
However, using this eqn. the volumes can be left in mL.

$$V_b = \frac{M_a * V_a}{M_b} = \frac{(0.100 \text{ M})(40.0 \text{ mL})}{(0.0400 \text{ M})} = \mathbf{100.0 \text{ mL NaOH}}$$

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5. (cont.)

b) (2 pts) What is the pH when 50.0 mL of NaOH has been added to the HCN solution?

This can be done in two ways.

1) **Neutralization rxn followed by common-ion problem:** determine the moles of acid, HCN, originally present and use the balanced eqn for the reaction of NaOH with the acid. (This is a stoichiometry problem as done in Chem 1210.

$$HCN + NaOH \longrightarrow Na^+ + CN^- + H_2O$$

$$(\text{Net Ionic Eqn.:}\quad HCN + OH^- \longrightarrow CN^- + H_2O)$$

This shows the reaction is 1:1, 1 mole of acid reacts with 1 mole of base.

Use a stoichiometry (BCA/ICC) table (looks like an ICE table but done using **moles**):

$$?\ \text{mol HCN} = 0.0400\ \text{L} \times \frac{0.100\ \text{mol HCN}}{1\ \text{L}} = 0.00400\ \text{mol HCN}$$

$$?\ \text{mol NaOH} = 0.0500\ \text{L} \times \frac{0.0400\ \text{mol NaOH}}{1\ \text{L}} = 0.00200\ \text{mol NaOH} = 0.00200\ \text{mol } OH^-$$

ICC (BCA) table:

(In **MOLES**)

	HCN	+	OH^-	$\rightarrow$	CN^-	+	H_2O
initial	0.00400		0.00200		0		
change	- 0.00200		- 0.00200		+ 0.00200		
comp.	0.00200		0		0.00200		

Total volume of soln at this point: 40.0 mL of HCN + 50.0 mL of NaOH = 90.0 mL

$$[HCN] = \frac{\text{mol HCN}}{V_T} = \frac{0.00200\ \text{mol HCN}}{0.0900\ \text{L}} = 0.0222\ \text{M HCN}$$

$$[CN^-] = \frac{\text{mol } CN^-}{V_T} = \frac{0.00200\ \text{mol } CN^-}{0.0900\ \text{L}} = 0.0222\ \text{M } CN^-$$

Same conc. (half-way to the eq. pt.) so this is a CI problem, more specifically a buffer soln. Could set up an ICE table but since it is a buffer soln use HH eqn.

$$pH = pK_a + \log\left(\frac{[CN^-]}{[HCN]}\right) = 9.3\underline{0}9 + \log\left(\frac{0.0222\ \text{M}}{0.0222\ \text{M}}\right) = 9.3\underline{0}9 = 9.\mathbf{31}\quad (\text{ only 2 s.f.})$$

$pH = pK_a$ when halfway to the eq. pt. (**Very weak acid so pH is already above 7 at the halfway pt.**)

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5. (cont.)

2) easier way:

It takes 100.0 mL of NaOH to get to the eq. pt. (see part A). We want the pH at 50.0 mL of NaOH. This is halfway to the eq. pt. This means half the HA has been converted to its conjugate base A^-. Thus the moles of HA and its conjugate base, A^-, are equal. Since they are in the same beaker their conc. are equal,

when halfway to eq. pt.: mol of HA = mol of A^- and $[HA] = [A^-]$

Looking at the HH eqn.,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = 9.3\underline{\mathbf{0}}9 + \log(1) = 9.3\underline{\mathbf{0}}9 = 9.\mathbf{31} \quad \text{(actually only 2 s.f.)}$$

$pH = pK_a$ when halfway to the eq. pt.

NOTE: This is a very weak acid and the pH at the half-way point is actually above pH = 7.

c) (4 pts) What is the **pH** at the **equivalence point**?

This isn't as hard as it seems. You need know what you get at the eq. pt. in the titration of a weak acid by a strong base. The following is the net ionic reaction which occurs during the titration between the acid being titrated and the titrant.

$$HCN + OH^- \longrightarrow CN^- + H_2O$$

Thus at the **eq. pt.** you get the **conjugate base** of the **WA** being titrated. This means you wind up with a **hydrolysis** problem (**salt solution** problem) involving an **anion**, a **weak base**. This requires an **ICE table** for a **base**.

$$CN^- + H_2O \rightleftarrows HCN + OH^-$$

This means the solution will be **BASIC** at the **eq. pt.** To calculate the pH you need the **concentration** of the **nitrite**, **CN^-**, at the **eq. pt.**. To get this you need the **moles** of **CN^-** & the **total volume** at the **eq. pt.**

Remember, all along the titration curve the moles of the acid, HA, remaining plus the moles of its conj. base, A^-, equals the total original moles of the acid, HA, at the start of the titration,

$(\text{mol of HA} + \text{mol of } A^-)_{\text{during titration}}$ = original mol HA before start of the titration

At the **eq. pt.** **<u>ALL</u>** the **original acid** present, HA, has been **converted** to its **conjugate base**, A^-, and the **total volume** **<u>equals</u>** the **volume of acid being titrated** and the **volume of titrant (base)** it takes to get to the **eq. pt.**

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5. (Cont.)

At eq. pt.: $(\text{mol A}^-)_{\text{eq. pt.}} = (\text{mol HA})_O$ (original moles of HA present)

$V_T = V_a + V_b$

Use $M_a * V_a = M_b * V_b$ to determine $V_{b,\text{titrant}}$ at eq. pt. and thus V_T

$$[\text{A}^-]_{\text{eq pt}} = \frac{\text{mol A}^-}{V_T} = \frac{\text{mol HA orig. present}}{V_T} = \frac{M_a * V_a}{V_a + V_b}$$

$$= \frac{(0.100\text{ M})\ (40.0\text{ mL})}{(40.0 + 100.0\ )\text{ mL}} = 0.028\underline{5}7\text{ M}$$

Now you can set up the ICE table for the hydrolysis (salt soln) problem at the eq. pt.:

	CN^-	+	H_2O	$\rightleftarrows$	HCN	+	OH^-
initial	$0.028\underline{5}7$				0		0
change	- x				+ x		+ x
equil	$0.028\underline{5}7$ - x				x		x

$$K_b = \frac{[\text{HCN}]\ [\text{OH}^-]}{[\text{CN}^-]} = \frac{x^2}{0.028\underline{5}7 - x} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.\underline{\mathbf{0}}40 \times 10^{-5}$$

Assume $0.028\underline{\mathbf{5}} \gg x$, so $(0.028\underline{\mathbf{5}} - x) \approx 0.028\underline{\mathbf{5}}$ $\quad \frac{x^2}{0.028\underline{5}7} = 2.\underline{\mathbf{0}}4 \times 10^{-5}$; $x = [\text{OH}^-] = 7.\underline{\mathbf{6}}3 \times 10^{-4}$

$$\%\text{ error} = \frac{7.\underline{\mathbf{6}}3 \times 10^{-4}}{0.028\underline{5}7} \times 100\% = 2.\underline{\mathbf{6}}7\ \%\text{ error}$$ (assumption above is valid)

pOH = $-\log(7.\underline{\mathbf{6}}3 \times 10^{-4}) = 3.\underline{\mathbf{12}}$ (2 s.f.)

pH = $14.00 - 3.\underline{\mathbf{12}} = 10.\underline{\mathbf{88}}$ (2 s.f.)

or

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{7.\underline{\mathbf{6}}3 \times 10^{-4}} = 1.\underline{\mathbf{3}}09 \times 10^{-11}$$

pH = $-\log(1.\underline{\mathbf{3}}09 \times 10^{-11}) = 10.\underline{\mathbf{88}}$

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5. (Cont.)

d) (4 pts) What is the **pH** at the point where 25.0 mL of NaOH has been added?

Can do two ways:

a) Do the neutralization reaction and corresponding stoichiometry problem to determine the moles of HA which have reacted and how many moles of A^- have been produced. You need to calculate moles of HA originally present and the moles of NaOH added and then moles of A^- produced by the neutralization rxn. This will produce some $A^-$and leave some excess HA (since the eq. pt. has not been reached yet).

$$HA + NaOH \longrightarrow Na^+ + A^- + H_2O$$

$$(\text{Net Ionic Eqn.: } HA + OH^- \longrightarrow A^- + H_2O)$$

This shows the reaction is 1:1, 1 mole of acid reacts with 1 mole of base.

Use a stoichiometry table (looks like an ICE table but done using **moles**):

	HA +	OH^- →	A^- +	H_2O	(In **MOLES**)
initial	0.00400	0.00100	0		
change	- 0.00100	- 0.00100	+ 0.00100		
comp.	0.00300	0	0.00100		

Total volume of soln at this point: 40.00 mL of HA + 25.0 mL of NaOH = 65.0 mL

$$[HA] = \frac{\text{mol HA}}{V_T} = \frac{0.00300 \text{ mol HA}}{0.0650 \text{ L}} = 0.046\underline{1}5 \text{ M HA}$$

$$[A^-] = \frac{\text{mol } A^-}{V_T} = \frac{0.0010 \text{ mol } A^-}{0.0650 \text{ L}} = 0.015\underline{3}8 \text{ M } A^-$$

This is a CI problem. Since the conc. are relatively large and the ratio is 0.25 it is more specifically a buffer soln. Could set up an ICE table but since it is a buffer soln use HH eqn. Can use moles in the ratio instead of molarities since the total volume of soln for the A^- and HA is the same and cancels.

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = 9.3\underline{0}9 + \log\left(\frac{0.015\underline{3}8 \text{ M}}{0.046\underline{1}5 \text{ M}}\right) = 8.8\underline{3}2 = \mathbf{8.\underline{83}} \quad \text{(actually only 2 s.f.)}$$

***** cont. next page *****

5. (Cont.)

b) Easier way:

When calculating the pH during a titration in the buffer region (most of the region of the pH curve) the problem is easier than above. When 25.0 mL of NaOH had been added the titration is 1/4 (25/100) of the way to the eq. pt. This means 1/4 (25/100) of the HA has been converted to A^- and 3/4 (75/100) of the HA remains. Use these ratios in the HH eqn.

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[A^-]}{[HA]}\right) = 9.3\underline{0}9 + \log\left(\frac{(25/100)}{(75/100)}\right)$$

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[A^-]}{[HA]}\right) = 9.3\underline{0}9 + \log\left(\frac{1}{3}\right) = 8.8\underline{3}2 = \mathbf{8.\underline{83}} \quad \text{(actually only 2 s.f.)}$$

NOTE: At this point in the titration it is to the left of the half-way point so $\mathrm{pH} < \mathrm{p}K_a$.

What is the **pH** at the point where 75.0 mL of NaOH has been added? (Not asked for in this problem.)

Can do two ways:

a) Do the neutralization reaction and corresponding stoichiometry problem to determine the moles of HA which have reacted and how many moles of A^- have been produced. You need to calculate moles of HA originally present and the moles of NaOH added and then moles of A^- produced by the neutralization rxn. This will produce some A^- and leave some excess HA (since the eq. pt. has not been reached yet). This is similar to what was done above when 25.0 mL of NaOH was added.

b) Easier way:

When calculating the pH during a titration in the buffer region (most of the region of the pH curve) the problem is easier than above. When 75.0 mL of NaOH had been added the titration is 3/4 (75/100) of the way to the eq. pt. This means 3/4 (75/100) of the HA has been converted to A^- and 1/4 (25/100) of the HA remains. Use these ratios in the HH eqn.

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[A^-]}{[HA]}\right) = 9.3\underline{0}9 + \log\left(\frac{(75/100)}{(25/100)}\right)$$

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[A^-]}{[HA]}\right) = 9.3\underline{0}9 + \log\left(\frac{3}{1}\right) = 9.7\underline{8}6 = \mathbf{9.\underline{79}} \quad \text{(actually only 2 s.f.)}$$

NOTE: At this point in the titration it is to the right of the half-way point so $\mathrm{pH} > \mathrm{p}K_a$.

***** cont. next page *****

I would suggest you look at the following 2 pages which is a general discussion of acid-base titrations.

5. (Cont.)

NOTE:

When dealing with titration problems it is often very useful to first determine where the eq. pt. is. That can make answering certain questions easier. There are 3 points on a titration curve (involving monoprotic acids or monoprotic bases, also called monobasic bases - accept 1 proton) which are discussed quite often and for which pH calculations are often done;

1) the start of the titration

Pretty easy for a strong acid or strong base (just a SA or SB problem - ch 16)
ICE table required if a WA or WB (again ch 16)

2) the eq. pt.

Real easy for a SA-SB or SB-SA involving a monoprotic acid
pH = 7 (salt soln problem for a neutral salt, such as NaCl - ch 16)
If titrating a WA or WB you should realize the range for the pH at the eq. pt.

At the eq. pt. for the titration involving monoprotic acids and monobasic (monoprotic) bases the following general statements about the pH of the solution can be made:

	pH at eq. pt.		Ex:	Resulting Salt
Strong acid - Strong base titration Strong base - Strong acid titration	= 7	(neutral)	HCl/NaOH KOH/HNO_3	NaCl KNO_3
Weak acid - Strong base titration	> 7	(basic)	HF/NaOH	NaF
Weak base - Strong acid titration	< 7	(acidic)	NH_3/HBr	NH_4Br

3) halfway to the eq. pt.

For a weak acid or weak base this is the easiest of the three since $pH=pK_a$ (buffer in which the conc. of the two components of the conjugate acid-base pair have equal concentrations so you use the HH eqn).

For a SA-SB or SB-SA titration you simply do a stoichiometry problem to calculate the excess strong acid or base left at the halfway pt. and account for dilution to get conc. of the strong acid or base.

***** cont. next page *****

5. (Cont.)

4) How about between the start of the titration and the eq. pt. (other than halfway)?

Technically once the titration begins and before the eq. pt. some of the acid or base you are titrating is being converted to its conjugate base or acid and some of the original acid or base being titrated remains. What has to be done is different if you are titrating a SA or SB or titrating a WA or WB. However, in either case you will need to do a stoichiometry problem (in moles) to determine how much of the original acid or base being titrated has been converted and how much remains (some will always remain until you reach the eq. pt.). If you are titrating a WA or WB you will then have a common-ion problem (which you will have along the titration curve between the start and eq. pt. - most of the time it turns out to be a buffer so you can use the HH eqn.)

In all cases for an acid being titrated by SB, between the start and eq. pt.:
(the moles of acid + the moles of its conj. base) = moles of acid originally present

In all cases for a base being titrated by SA, between the start and eq. pt.:
(the moles of base + the moles of its conj. acid) = moles of base originally present

a) SA-SB titration (SA being titrated by SB):

Neutralization rxn (stoich. problem): determine how much SA has been neutralized (reacted with the SB being added & converted to its conj. base) and how much remains - don't forget dilution

Ex: $HCl + NaOH \rightarrow Na^+ + Cl^- + H_2O$

b) SB-SA titration: similar to above but doing calc. for neutralization of SB.

c) WA-SB titration: (WA being titrated by SB):

Technically you must do a neutralization reaction (in moles) involving the reaction of the WA with the SB first to determine how much of the WA (HA below) has been converted to it's conjugate base (A-):

Ex: $HA + NaOH \rightarrow Na^+ + A^- + H_2O$

This would then have to be followed by a common-ion problem. Depending on how much WA has been converted to its conj. base it could wind up being a buffer so you could use the Henderson-Hasselbalch eqn. How would you know? If the ratio of moles of base, A^-, to moles of conj. acid, HA, is between 10 and 0.1 you can generally use the HH eqn.

There is a way to do this easily if you know you are in the buffer region. As discussed in lecture if you know where the eq. pt. is (i.e. the volume of titrant it takes to get to the eq. pt.) it's pretty easy to calculate the pH in the buffer region using the HH eqn. You can simply use ratios of volumes in the place of the ratio of base to acid ($[A^-]/[HA]$).

For example using a WA-SB titration, lets say it takes 50 mL of SB (titrant) to reach the eq. pt. If you want to calculate the pH after 10 mL of SB have been added you are 10/50 of the way to the eq. pt.. This means 10/50 of HA (the weak acid being titrated) has been converted to its conjugate base, A^-, and 40/50 of HA remains.

You can then use the HH eqn using these ratios,

$pH = pK_a + \log([A-]/[HA]) = pK_a + \log\{(10/50)/(40/50\} = pK_a + \log\{10/40\}$

What if you've added 12.5 mL of SB (titrant)? Then you have

$pH = pK_a + \log([A-]/[HA]) = pK_a + \log\{(12.5/50)/(37.5/50\} = pK_a + \log\{12.5/37.5\}$

6. (8 pts) 15.0 mL of 0.100 M CH_3NH_2 is titrated with 0.035 M HCl. ($K_b = 4.4 \times 10^{-4}$)
Show work or explain!
a) (2 pts) How many mL of HCl are required to reach the **equivalence point**?

Remember, at the eq. pt.: moles H^+ = moles OH^- (this is often stated as moles acid = moles of base but what I have is a more accurate statement)

This is a monoprotic weak base (accepts one proton, also referred to as a monobasic base) being titrated by a strong acid. So it's a 1:1 ratio for the titration.

This can be done in two ways.

1) determine the moles of base, CH_3NH_3, originally present and use the balanced eqn for the reaction of HCl with the base. (This is a stoichiometry problem as done in Chem 1210.)

$CH_3NH_2 + HCl \longrightarrow CH_3NH_3^+ + Cl^-$ (neutralization rxn during titration)

(Net Ionic Eqn.: $CH_3NH_2 + H^+ \longrightarrow CH_3NH_3^+$)

This shows the reaction is 1:1, 1 mole of base reacts with 1 mole of acid.

NOTE: For the sake of simplicity I will use B for CH_3NH_2 and HB+ for $CH_3NH_3^+$

$$? \text{ mL HCl} = 0.0150 \text{ L B soln} \times \frac{0.100 \text{ mol B}}{1 \text{ L B soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol B}} \times \frac{1 \text{ L HCl soln}}{0.035 \text{ mol HCl}} \times \frac{10^3 \text{ mL}}{1 \text{ L}}$$

= **4$\underline{2}$.85 mL HCl** (2 s.f.)

2) easier way:

moles H^+ = moles OH^-

moles acid = moles base

$M_a * V_a = M_b * V_b$ (Technically molarity of H^+ and molarity of OH^-.)

M_a & V_a correspond to the HCl used for the titration (the titrant)
M_b & V_b correspond to the weak base being titrated

For a weak acid being titrated by a strong base this would be flipped (M_a and V_a would correspond to the weak acid being titrated and M_b and V_b would correspond to the strong base, the titrant).

Technically to get moles V would be in liters.
However, using this eqn. the volumes can be left in mL.

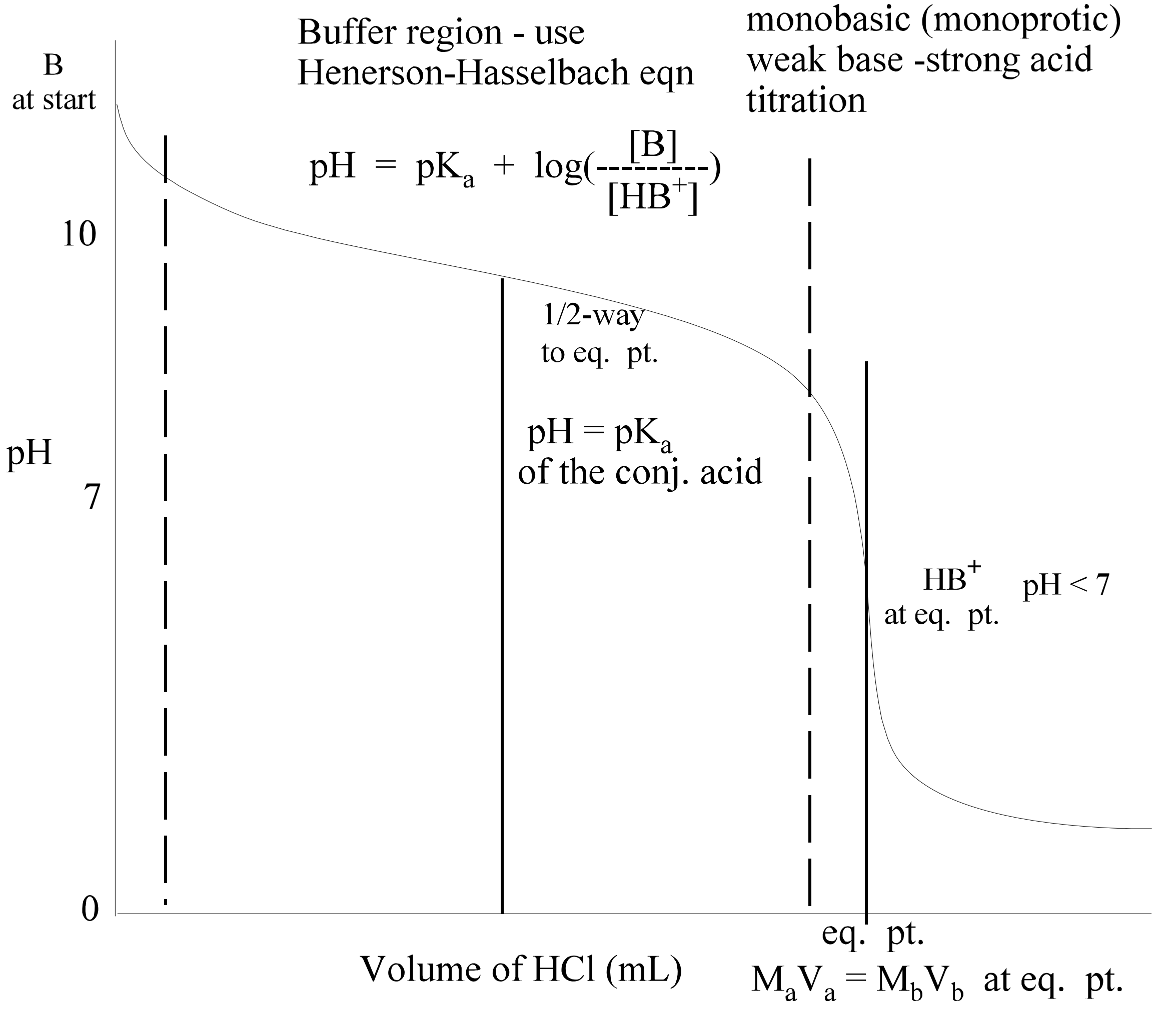
$$V_a = \frac{M_b * V_b}{M_a} = \frac{(0.100 \text{ M})(15.0 \text{ mL})}{(0.035 \text{ M})} = \mathbf{4\underline{2}.85 \text{ mL HCl}}$$

***** cont. next page *****

6. (Cont.)

b) (2 pts) Sketch the titration curve and clearly mark the **pH** at the **equivalence point**. (less than 7, equal to 7 or greater than 7).

The following is a general titration curve for a monoprotic weak base being titrated by a strong acid.



M_aV_a refers to the HCl titrant & M_bV_b refers to the weak base

***** cont. next page *****

6. (Cont.)

c) (4 pts) What is the **pH** at the **equivalence point**?

This isn't as hard as it seems. You need know what you get at the eq. pt. in the titration of a weak base by a strong acid. The following is the net ionic reaction which occurs during the titration between a monoprotic WB being titrated and the SA titrant. As above, I'm using B for the monoprotic WB and HB^+ for its conjugate acid.

$$B + H^+ \longrightarrow HB^+$$

Thus, at the **eq. pt.** you get the **conjugate acid** of the **WB** being titrated. This means you wind up with a **hydrolysis** problem (**salt solution** problem) involving a **cation**, a **weak acid**. This requires an **ICE table** for an **acid**.

$$HB^+ \rightleftarrows H^+ + B$$

The solution will be **ACIDIC** at the **eq. pt.** To calculate the pH you need the **concentration** of the **conjugate acid of the weak base**, **HB^+**, at the **eq. pt.**. To get this you need the **moles** of **HB^+** & the **total volume** at the **eq. pt.**

Remember, all along the titration curve the total moles of the base, B, in excess, plus the moles of its conj. acid, HB^+, equals the total original moles of the base, B, at the start of the titration,

$$(\text{mol of B} + \text{mol of HB}^+)_{\text{during titration}} = \text{original mol B before start of the titration}$$

At the **eq. pt.** **<u>ALL</u>** the **original base** present, B, has been **converted** to its **conjugate acid**, HB^+, and the **total volume <u>equals</u>** the **volume of base being titrated** and the **volume of titrant (acid)** it takes to get to the **eq. pt.**

At eq. pt.: $(\text{mol HB}^+)_{\text{eq pt}} = (\text{mol B})_{\text{original}}$ (original moles of B present)

$V_T = V_b + V_a$

Use $M_a * V_a = M_b * V_b$ to determine $V_{a,\ \text{titrant}}$ at eq. pt. and thus V_T

$$[HB^+]_{\text{eq pt}} = \frac{(\text{mol HB}^+)_{\text{eq pt}}}{V_T} = \frac{(\text{mol B})_{\text{orig. present}}}{V_T}$$

$$= \frac{M_b * V_b}{V_b + V_a}$$

M_b = molarity of B
V_b = volume of B at start of titration
V_a = volume of HCl added

$$= \frac{(0.100\ \text{M})\ (15.00\ \text{mL})}{(15.00 + 4\underline{2}.85\ )\ \text{mL}}$$

$$= 0.02\underline{5}92\ \text{M}$$

***** **continued on next page** *****

6. (Cont.)

At the eq. pt. there's HB^+ in H_2O. This is a **hydrolysis problem** (salt solution problem). Since HB^+ is a cation (conj. acid of the base being titrated) it will act as an acid and the solution will be acidic.

HB^+ is conj acid of weak base B - acid equil problem - **Use ICE (equil.) table** (in Molarity)

	HB^+	$\rightleftarrows$	B	+	H^+
initial	$0.02\underline{5}92$		0		0
change	- x		+ x		+ x
equil	$0.02\underline{5}92$ - x		x		x

$$K_a = \frac{[B\,[H^+]}{[HB^+]} = \frac{x^2}{0.02\underline{5}92 - x} = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-4}} = 2.\underline{2}72 \times 10^{-11}$$

Assume $0.02\underline{5}92 >> x$, so $(0.02\underline{5}92 - x) \approx 0.02\underline{5}92$

$$\frac{x^2}{0.02\underline{5}92} = 2.\underline{2}72 \times 10^{-11}$$

$x = [H^+] = 7.\underline{6}76 \times 10^{-7}$

$$\% \text{ error} = \frac{7.\underline{6}76 \times 10^{-7}}{0.02\underline{5}92} \times 100\% = 0.00296\ \% \text{ error}$$ (very good assumption that "x" was small)

$pH = 6.1\underline{1}48 = \mathbf{6.11}$ at the eq. pt.

ACIDIC (as it should be)

NOTE:

Real easy for a SA-SB or SB-SA involving a monoprotic acid
pH = 7 (salt soln problem for a neutral salt, such as NaCl - ch 16)
If titrating a WA or WB you should realize the range for the pH at the eq. pt.

At the eq. pt. for the titration involving monoprotic acids and monobasic (monoprotic) bases the following general statements about the pH of the solution can be made:

	pH at eq. pt.	Ex:	Resulting Salt
Strong acid - Strong base titration	= 7 (neutral)	HCl/NaOH	NaCl
Strong base - Strong acid titration		KOH/HNO_3	KNO_3
Weak acid - Strong base titration	> 7 (basic)	HF/NaOH	NaF
Weak base - Strong acid titration	< 7 (acidic)	NH_3/HBr	NH_4Br

7. Which of the following equations is the "Bruce" equation as named during lecture?

$$M_a * V_a = M_b * V_b$$ (Technically molarity of H^+ and molarity of OH^-.)

M_a & V_a correspond to the acid being titrated
M_b & V_b correspond to the strong base used for the titration (the titrant)

(Vice versa when a base is titrated by a strong acid.)

We called this eqn. “Bruce**” in lecture. This was meant as a reward to those coming to lecture.**

This looks like the dilution equation but there is a difference.

$$M_2 * V_2 = M_1 * V_1$$

M_1 & V_1 correspond to the initial molarity and initial volume.
M_2 & V_2 correspond to the final molarity and final TOTAL volume.

There were two problems on the quiz directly dealing with this eqn, one asking for the volume of strong base titrant for a WA-SB titration and one asking for the volume of strong acid titrant for a WB-SA titration.

8. (3 pts) You have a saturated solution of $Mg_3(PO_4)_2$. It follows that

a) $[Mg^{2+}] < [PO_4^{3-}]$
b) $[Mg^{2+}] = (K_{sp})^{1/5}$
c) $[Mg^{2+}] = 3/2\,(K_{sp})^{1/5}$
d)* $[Mg^{2+}] = 3/2\,[PO_4^{3-}]$
e) $[Mg^{2+}] = 2/3\,[PO_4^{3-}]$

You're looking for some relationship between the concentrations of each ion and K_{sp}. It's a good idea to write the equilibrium reaction. That will make it easier to see how the conc. of each ion is related to the molar solubility, each other and to K_{sp}.

	$Mg_3(PO_4)_2$ (s)	$\rightleftarrows$	$3\ Mg^{2+}$ (aq)	+	$2\ PO_4^{3-}$ (aq)
I	----		0 M		0 M
C	- x		+ 3x		+ 2x
E	----		3x		2x

x is the molar solubility of $Mg_3(PO_4)_2$

$[Mg^{2+}] = 3x$

$[PO_4^{3-}] = 2x$

$K_{sp} = [Mg^{2+}]^3\,[PO_4^{3-}]^2$

$(3x)^3 * (2x)^2$

$27x^3 * 4x^2$

$K_{sp} = 108\,x^5$

$x = (K_{sp}/108)^{1/5}$ This is the molar solubility of $Mg_3(PO_4)_2$.

How are the conc. of Mg^{2+} and PO_4^{3-} related? You can use the "change" line in the ICE table to see this. That line shows a 3:2 ratio of Mg^{2+} to PO_4^{3-} . You can also do the following,

$$\frac{[Mg^{2+}]}{[PO_4^{3-}]} = \frac{3x}{2x} = \frac{3}{2}$$

$[Mg^{2+}] = (3/2)\,[PO_4^{3-}]$

Also,

$[Mg^{2+}] = 3x = 3\,(K_{sp}/108)^{1/5}$

$[PO_4^{3-}] = 2x = 2\,(K_{sp}/108)^{1/5}$

9. (3 pts) Which compound is more soluble in water, $Mn(OH)_2$ ($K_{sp} = 1.6 \times 10^{-13}$) or $SrCO_3$ ($K_{sp} = 9.3 \times 10^{-10}$)? **Show all work and explain!**

Calculate the molar solubility for each compound using the K_{sp}.

In Ch 16 you could compare K_a values of two acids to determine which is the stronger acid because K_a expressions for all weak acids look the same (the same applies to weak bases). Using K_{sp} values to compare solubilities of different salts is not as straightforward because they don't all have the form of the expression for K_{sp}. If the K_{sp} expressions are the same you could use the value of K_{sp} to compare the solubilities. In this case, you can't tell just by looking at the size of K_{sp} because the form of each is different.

$Mn(OH)_2$ $K_{sp} = [Mn^{2+}]\,[OH^-]^2$

$SrCO_3$ $K_{sp} = [Sr^{2+}]\,[CO_3^{2-}]$

	M_yA_z (s)	⇄	$y\,M^{z+}$ (aq)	+	$z\,A^{y-}$ (aq)
I	----		0 M		0 M
C	- x		+ y•x		+ z•x
E	----		y•x		z•x

$$K_{sp} = [y \bullet x]^y\,[z \bullet x]^z$$

$Mn(OH)_2$ $K_{sp} = [Mn^{2+}]\,[OH^-]^2 = (x)(2x)^2 = 4x^3 = 1.6 \times 10^{-13}$
$x = 3.4 \times 10^{-5}$

$SrCO_3$ $K_{sp} = [Sr^{2+}]\,[CO_3^{2-}] = (x)(x) = x^2 = 9.3 \times 10^{-10}$
$x = 3.0 \times 10^{-5}$

Thus, $Mn(OH)_2$ is more soluble (even though the K_{sp} is smaller).

For something like AgCl, which is 1:1 ratio you could simply compare it's K_{sp} to the K_{sp} for $SrCO_3$ to determine which was more (or less) soluble because the K_{sp}'s have the same form.

AgCl $K_{sp} = [Ag^+]\,[Cl^-] = (x)(x) = x^2 = 1.8 \times 10^{-10}$
$x = 1.3 \times 10^{-5}$ M

Note: You can simply compare K_{sp} values for AgCl and $SrCO_3$ in this case since they have the same form. $SrCO_3$ is more soluble than AgCl since the K_{sp} for $SrCO_3$ is larger than the K_{sp} for AgCl

10. (3 pts) Which of the following salts will be substantially more soluble in acidic solution than in pure water?

1) $Ca_3(PO_4)_2$ 2) AgCl 3) CuBr **4) $BaSO_4$** 5) **PbF_2**

Look at the solubility reaction of a salt:

$$M_yX_z \rightleftarrows y\,M^{z+} + z\,X^{y-} \qquad (1)$$

where M is a cation and X is an anion.

Now look at the reaction of H^+ with an anion. Anions which can act as basses will react with acids, H^+,

$$X^- + H^+ \rightleftarrows HX \qquad (2)$$

If X^- is OH^-, a strong base (such as O^{2-}, S^{2-}, etc.) or a weak base (the conjgate base of a weak acid) this reaction will occur. This reaction then removes X^- from the dissolution reaction (1). According to Le Châtelier's principle, if a product is removed the reaction will shift right, in the forward direction, TOWARD REMOVED, to replace it. This means more of the salt will dissolve, increasing its solubility. If X^- is the conjugate base of a strong acid (Cl^-, Br^-, I^-, NO_3^-, ClO_3^-, ClO_4^- and HSO_4^-) this reaction doesn't occur. So if the base portion of the salt is the conj. base of a strong acid lowering the pH (making the soln acidic) will not make it more soluble than in pure water.

1) $Ca_3(PO_4)_2\,(s) \rightleftarrows 2\,Ca^{2+}\,(aq) + 2\,PO_4^{3-}\,(aq)$

$H^+\,(aq) + PO_4^{3-}\,(aq) \rightleftarrows HPO_4^{2-}\,(aq)$

This rxn removes PO_4^{3-} from the first rxn causing the first rxn to shift to the right. As it does more of the $Ca_3(PO_4)_2$ dissolves and **solubility increases**. More soluble in acidic soln.

4) $BaSO_4\,(s) \rightleftarrows Ba^{2+}\,(aq) + 2\,SO_4^{2-}\,(aq)$

$H^+\,(aq) + SO_4^{2-}\,(aq) \rightleftarrows HSO_4^-\,(aq)$

This rxn removes SO_4^{2-} from the first rxn causing the first rxn to shift to the right. As it does more of the $BaSO_4$ dissolves and **solubility increases**. More soluble in acidic soln.

5) $PbF_2\,(s) \rightleftarrows Pb^{2+}\,(aq) + 2\,F^-\,(aq)$

$H^+\,(aq) + F^-\,(aq) \rightleftarrows HF\,(aq)$

Similar to #4 above. Solubility increases in acid.

2) $AgCl\,(s) \rightleftarrows Ag^+\,(aq) + Cl^-\,(aq)$

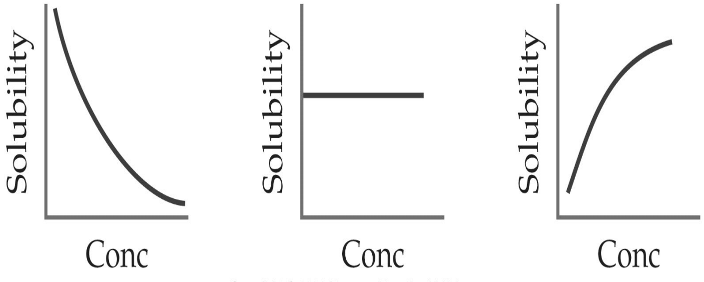
$H^+\,(aq) + Cl^-\,(aq) \rightleftarrows$ NO RXN (would get HCl, a strong acid)

This rxn does not occur (would get a strong acid, which completely ionizes, so the HCl does not form). Thus, this rxn does NOT remove Cl^- from the first rxn. This means adding acid will NOT increase the solubility of the salt.

The same applies to #3, CuBr (Br^- is the conj. base of HBr).

11. (3 pts) Solutions of strontium carbonate, $SrCO_3$, were prepared. The graphs below represent the effects on the solubility of strontium carbonate in the presence of various additives: hydrochloric acid, strontium nitrate and potassium chloride (conc. of additive on x-axis). Match the additives to the graphs to account for the solubility behavior: K_{sp} for $SrCO_3$ is 9.3×10^{-10}.

Three solutions of $SrCO_3$ are prepared. Then three different substances, hydrochloric acid (HCl), strontium nitrate ($Sr(NO_3)_2$) and potassium chloride (KCl) are added to each of the three $SrCO_3$ solutions. Match the additive to the graphs to account for the solubility behavior.



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$Sr(NO_3)_2$ KCl HCl

Graph 1: The solubility of the $BaCO_3$ decreases as the conc. of the additive increases (as amount of additive inc.). Think common-ion effect.

$$SrCO_3\ (s) \rightleftarrows Sr^{2+}\ (aq) + CO_3^{2-}\ (aq)$$

If either Sr^{2+} or CO_3^{2-} is added the solubility of the solid will decrease. Thus the additive must be strontium nitrate, $Sr(NO_3)_2$.

Graph 2: The solubility of the $SrCO_3$ remains constant as the conc. of the additive increases (as amount of additive inc.). If you think about the potassium chloride (KCl) it gives K^+ and Cl^-, neither of which reacts with the Sr^{2+} or CO_3^{2-}. Thus this additive has no effect on the solubility.

Graph 3: The solubility of the $SrCO_3$ increases as the conc. of the additive increases (as amount of additive inc.). This occurs for the HCl, a strong acid. The strong acid reacts with the CO_3^{2-} since it is a weak base (an anion which acts as a weak base since it is not the conjugate base of a strong acid).

$$CO_3^{2-}\ (aq) + H^+\ (aq) \rightleftarrows HCO_3^-\ (aq)$$

This reaction removes the CO_3^{2-} from solution thus removing a product from the solubility reaction making it shift to the right so more of the $SrCO_3(s)$ dissolves. You can see that by adding the two reactions to get an overall reaction.

$$SrCO_3\ (s) \rightleftarrows Sr^{2+}\ (aq) + CO_3^{2-}\ (aq)$$

$$CO_3^{2-}\ (aq) + H^+\ (aq) \rightleftarrows HCO_3^-\ (aq)$$

$$SrCO_3\ (s) + H^+\ (aq) \rightleftarrows Sr^{2+}\ (aq) + HCO_3^-\ (aq)$$

This overall eqn shows the affect of the H^+ (strong acid) on the $SrCO_3$. With enough strong acid added the HCO3- will react with the excess H+ to drive the reaction even further to the right and you would have this overall reaction,

$$SrCO_3\ (s) + 2H^+\ (aq) \rightleftarrows Sr^{2+}\ (aq) + H_2CO_3\ (aq)$$

12. (15 pts) For CaF_2, $K_{sp} = 3.9 \times 10^{-11}$ and for HF, $K_a = 6.8 \times 10^{-4}$. (Show ICE or stoichiometry tables, state any assumptions made and check the percent error.)

a) (3 pts) Calculate the molar solubility of CaF_2 in pure water.

Need to write the equilibrium eqn. associated with the dissolution of CaF_2.

$$CaF_2\,(s) \rightleftarrows Ca^{2+}\,(aq) + 2\,F^-\,(aq)$$

$$K_{sp} = [Ca^{2+}]\,[F^-]^2$$

The solubility of CaF_2 in H_2O can be found in the following way (set up an ICE table):

	CaF_2 (s)	$\rightleftarrows$	Ca^{2+} (aq)	+	$2\,F^-$ (aq)
I	----		0 M		0 M
C	- x		+ x		+ 2x
E	----		x		2x

$$K_{sp} = \underset{(x)}{[Ca^{2+}]}\,\underset{(2x)^2}{[F^-]^2} = 3.9 \times 10^{-11}$$

$$4\,x^3 = 3.9 \times 10^{-11}$$

$$x = 2.\underline{1}36 \times 10^{-4}\ M$$

$$x = 2.\underline{1} \times 10^{-4}\ M \quad \text{(molar solubility in water)}$$

***** cont. next page *****

12. (Cont.)

b) (5 pts) Calculate the molar solubility of CaF_2 in the presence of 0.010 M NaF.

This is a common-ion problem:

$$CaF_2\,(s) \rightleftarrows Ca^{2+}\,(aq) + 2\,F^-\,(aq)$$

I	----	0 M	0.010 M
C	- x	+ x	+ 2x
E	----	x	0.010 + 2x

$$K_{sp} = [Ca^{2+}]\,[F^-]^2 = 3.9 \times 10^{-11}$$

$$(x)\;(0.010 + 2x)^2 = 3.9 \times 10^{-11}$$

This reaction does not go very far to the right, so we will ignore the "2x" in the (0.010 + 2x)

$$(x)\,(0.010)^2 = 3.9 \times 10^{-11}$$

$$x = 3.9 \times 10^{-7}\ M$$

$$\%\ error = \frac{2(3.9 \times 10^{-7})}{0.010} \times 100\% = 0.0078\ \%\ error \quad \text{(assumption above is valid)}$$

(assumption of ignoring "2x" is good, very small compared to 0.010)

This is the molar solubility of CaF_2 in a soln with 0.010 M NaF (in the presence of the common ion, F^-). Note the **solubility <u>decreased</u>** in the presence of the common ion, F^-, as it should based on Le Chatelier's Principle. Add a product and the rxn shifts left, toward the reactant, so get more reactant, the solid CaF_2, so less dissolves (solubility decreases).

c) (7 pts) Calculate the molar solubility of CaF_2 in the presence of 2.0 M HCl.

CaF_2 dissolves to give Ca^{2+} and F^-. The F^- is the conjugate base of a weak acid (HF) and will therefore act like a weak base. That means it will react with strong acid (H^+) to form HF. That means as H^+ is added to the CaF_2 soln. the H^+ from the strong acid reacts with the F^- to form HF thus removing the F^- from the CaF_2 equilibrium thus causing it to shift right (toward removed - toward product since a product was removed).

Lets see how this works with the equilibria equations.

$$CaF_2\,(s) \rightleftarrows Ca^{2+}\,(aq) + 2\,F^-\,(aq) \qquad K_{sp}$$

$$H^+\,(aq) + F^-\,(aq) \rightleftarrows HF\,(aq) \qquad K = K_a^{-1}$$

(This is the revers of the K_a rxn, $HF\,(aq) \rightleftarrows H^+\,(aq) + F^-\,(aq)$)

We actually also need to multiply the 2nd eqn. by 2 (multiply K_a eqn by -2) so we have the following:

$$CaF_2\,(s) \rightleftarrows Ca^{2+}\,(aq) + 2\,F^-\,(aq) \qquad K_{sp}$$

$$2\,H^+\,(aq) + 2\,F^-\,(aq) \rightleftarrows 2\,HF\,(aq) \qquad K = K_a^{-2}$$

***** cont. next page *****

12(c). (Cont.)

Add the two eqns. to see the overall rxn for CaF_2 and H^+ (multiply the Ks)

$$\begin{array}{lcl}
CaF_2\,(s) \;\rightleftarrows\; Ca^{2+}\,(aq) \;+\; 2\,F^-\,(aq) & \qquad & K_{sp} \\
2\,H^+\,(aq) \;+\; 2\,F^-\,(aq) \;\rightleftarrows\; 2\,HF\,(aq) & \qquad & K_2 = K_a^{-2} \\
\hline
\end{array}$$

$$CaF_2\,(s) \;+\; 2\,H^+\,(aq) \;\rightleftarrows\; Ca^{2+}\,(aq) \;+\; 2\,HF\,(aq)$$

$$K = K_{sp} \bullet K_a^{-2} = (3.9 \times 10^{-11})\,(6.8 \times 10^{-4})^{-2} = 8.434 \times 10^{-5}$$

Set up an ICE table:

	$CaF_2\,(s)$ +	$2\,H^+\,(aq)$ $\rightleftarrows$	$Ca^{2+}\,(aq)$ +	$2\,HF\,(aq)$
I	----	2.0 M	0 M	0 M
C	- x	- 2x	+ x	+ 2x
E	----	(2.0 - 2x)	x	2x

$$K = \frac{[Ca^{2+}]\,[HF]^2}{[H^+]^2} = 8.434 \times 10^{-5}$$

$$K = \frac{(x)\,(2x)^2}{(2.0 - 2x)^2} = 8.434 \times 10^{-5}$$

This reaction does not go very far to the right, so we will ignore the “2x” in the (2.0 - 2x)

$$K = \frac{(x)\,(2x)^2}{(2.0)^2} = 8.434 \times 10^{-5}$$

$$x = 4.\underline{\mathbf{3}}85 \times 10^{-2}\ M = 4.\underline{\mathbf{4}} \times 10^{-2}\ M$$

This is the molar solubility of CaF_2 in 2.0 M HCl. You can see the solubility increased in acid compared to the solubility in pure water ($4.\underline{\mathbf{4}} \times 10^{-2}$ M compared to $2.\underline{\mathbf{1}} \times 10^{-4}$ M).

The % error in assuming $2x \ll 2.0$ is:

$$\%\ error = \frac{2.0 - (2.0 - 2x)}{2.0} * 100 = \frac{2x}{2.0} * 100 = \frac{2\,(4.\underline{\mathbf{3}}85 \times 10^{-2})}{2.0} * 100 = 4.385\ \%$$

The assumption is valid (barely).

13. (6 pts) Calculate the concentration of free Cd^{2+} ions in a solution made by adding 0.010 moles of $Cd(NO_3)_2$ to 1.0 L of a 2.0 M NaBr solution. $K_f = 5 \times 10^3$ for $CdBr_4^{2-}$
(Show ICE or stoichiometry tables, state any assumptions made and check the percent error.)

NOT on quiz, just for practice.

This a complex-ion formation problem. The equilibrium rxn for this case is:

$$Cd^{2+}(aq) \quad + \quad 4\,Br^-(aq) \quad \rightleftarrows \quad CdBr_4^{2-}(aq) \qquad K_f$$

The equilibrium constant has a special symbol, K_f, and name, **formation constant**, and it is associated with the formation of a **complex ion** from the corresponding constituents, a **metal ion** and **complexing ion**. The **complexing ion** is a **Lewis Base** (the metal acts as a Lewis Acid) and is often referred to as a **ligand**. The corresponding complex ion is soluble in solution. The K_f values for most complex ions are quite large. This means in solution most of the metal is often in the form of the complex ion. Often times we make the assumption that the complex ion forms completely. Thus, you need to find whether the metal or ligand is the limiting reactant to determine how much complex ion forms. Then you look to see how much of it comes apart in solution to give free metal ion.

a) Since K_f is so large assume the metal ion and ligand reaction goes to completion. Do a stoichiometry problem (ICE/BCA table in moles) to see which is the limiting reactant and find the conc. of the complex ion (the product). The volume of solution is 1.0 L for this problem so the moles of the Cd^{2+} and Br^- are equal to their molarities.

ICC (BCA) table (**in moles**)

	Cd^{2+} (aq)	+	4 Br^- (aq)	⇄	$CdBr_4^{2-}$(aq)
I	0.010		2.0		0
C	- 0.010		- 4(0.010)		+ 0.010
C	0		1.96 mol		+ 0.010 mol

Technically, all of these moles are approximate but will be very close to their final values, particularly for the Br^- and the complex, $CdBr_4^{2-}$.

b) Now determine how much of the complex ion dissociates. Use the dissociation constant, K_d, for the complex ion, which is simply the inverse of K_f and the reaction is the reverse of the formation reaction.

Need the conc. of the complex, $CdBr_4^{2-}$, and the remaining Br^-. Since the volume of the Br^- (NaBr) solution is 1.0 L to start with and the addition of the small amount of $Cd(NO_3)_2$ won't change the volume appreciably the volume of the soln is still 1.0 L.

$[Br^-] = 1.96$ M

$[CdBr_4^{2-}] = 0.010$ M

***** cont. next page *****

13. (cont.)

	$CdBr_4^{2-}(aq)$	$\rightleftarrows$	$Cd^{2+}(aq)$	+	$4\ Br^-(aq)$
I	0.010 M		0 M		1.96 M
C	- x		+ x		+ 4 x
E	0.010 - x		+ x		1.96 + 4 x

$$K_d = \frac{[Cd^{2+}][Br^-]^4}{[CdBr_4^{2-}]} = 1/(5.0 \times 10^3) = 2.0 \times 10^{-4}$$

$$K_d = \frac{(x)(1.96 + 4x)^4}{(0.010 - x)} = 2.0 \times 10^{-4}$$

Since K_d is relatively small assume "x" << 0.010 and "4x" << 1.96

$$K_d = \frac{(x)(1.96)^4}{(0.010)} = 2.0 \times 10^{-4} \qquad x = [Cd^{2+}] = 1.\underline{3}55 \times 10^{-7} = \mathbf{1.4 \times 10^{-7}}\ M$$

The % error in assuming x << 0.10 is:

$$\%\ error = \frac{\mathbf{1.4 \times 10^{-7}}}{0.010} * 100 = 1.36 \times 10^{-3}\ \%$$

(Don't need to check "4x" << 1.96 since this is ok)

The final conc. of free Cd^{2+} is **1.4×10^{-7}** M and is very close to the "0" it was approximated to be in the K_f rxn. we started with.

14. (6 pts) Calculate the molar solubility of $Al(OH)_3$ in 3.0 M NaOH. **Show ALL work & explain!**
K_{sp} ($Al(OH)_3$) = 4.6 x 10^{-33} K_f ($Al(OH)_4^-$) = 1.1 x 10^{33}

Calculate conc. of a compound involving a metal cation which also forms a complex ion in solution. In this case this is an amphoteric cation (Al^{3+}, Cr^{3+}, Sn^{2+} and Zn^{2+} are the most common ones you'll see). Hydroxides and oxides of these cations can act as and acid or base. The solubility of these is strange in that like all hydroxides they're more soluble in acidic solution than pure water but unlike most will also be more soluble in basic solution than pure water because they form a soluble complex with OH^-. Thus, going from an acidic solution to basic solution the solubility first decreases to a minium as base is added to an acidic solution (form the insoluble hydroxide from the metal cation as OH^- is added) and then the solubility increases again as the conc. of OH^- is increases and the soluble complex is formed.

$$Al(OH)_3\,(s) \rightleftarrows Al^{3+}\,(aq) + 3\,OH^-\,(aq) \qquad K_{sp} = 4.6 \text{ x } 10^{-33}$$

$$Al^{3+}\,(aq) + 4\,OH^-\,(aq) \rightleftarrows Al(OH)_4^-\,(aq) \qquad K_f = 1.1 \text{ x } 10^{33}$$

$$Al(OH)_3\,(s) + OH^-\,(aq) \rightleftarrows Al(OH)_4^-\,(aq)$$

$$K = K_{sp} \bullet K_f = (4.6 \text{ x } 10^{-33})\,(1.1 \text{ x } 10^{33}) = 5.\underline{0}6$$

This value for K indicates significant amounts of reactants and products at equilibrium.

$[OH^-] = [NaOH] = 3.0$ M

	$Al(OH)_3\,(s)$	+	$OH^-\,(aq)$	$\rightleftarrows$	$Al(OH)_4^-\,(aq)$
initial	---		3.0		0
change	- x		- x		+ x
equil			3.0 - x		x

$$K = \frac{[Al(OH)_4^-]}{[OH^-]} = \frac{x}{(3.0 - x)} = 5.\underline{0}6$$

Can not assume "x" is small compared to 3.0 since K is not small. Don't have to since this is easy to solve, as it's a linear equation. When you have a linear equation you should solve it and not assume "x" is small.

$x = 2.\underline{5}04$ M $= 2.\underline{5}$ M

15. (5 pts) The K_f for the complex ion $Ag(S_2O_3)_2^{3-}$ is 2.9×10^{13}. The K_{sp} for AgI is 8.5×10^{-17}. What is the molar solubility of AgI in a solution that is made by adding $Na_2S_2O_3$ to make the solution 2.0 M in $Na_2S_2O_3$? (Show ICE or stoichiometry tables, state any assumptions made and check the percent error.)

This type of question was not on the Carmen quiz. It's just thrown in for practice.

Calculate conc. of a compound involving a metal cation which also forms a complex ion in solution.

$$AgI\,(s) \rightleftarrows Ag^+\,(aq) + I^-\,(aq) \qquad K_{sp} = 8.5 \times 10^{-17}$$

$$Ag^+\,(aq) + 2\,S_2O_3^{2-}\,(aq) \rightleftarrows Ag(S_2O_3)_2^{3-}\,(aq) \qquad K_f = 2.9 \times 10^{13}$$

$$AgI\,(s) + 2\,S_2O_3^{2-}\,(aq) \rightleftarrows Ag(S_2O_3)_2^{-}\,(aq) + I^-\,(aq)$$

$$K = K_{sp} \bullet K_f = (8.5 \times 10^{-17})(2.9 \times 10^{13}) = 2.\underline{4}65 \times 10^{-3}$$

This value for K indicates mostly reactants at equilibrium.

	AgI (s) +	$2\,S_2O_3^{2-}$ (aq) ⇄	$Ag(S_2O_3)_2^{3-}$ (aq) +	I^- (aq)
initial	---	2.0	0	0
change	- x	- 2x	+ x	+ x
equil	---	2.0 - 2x	x	x

$$K = \frac{[Ag(S_2O_3)_2^{3-}]\,[I^-]}{[S_2O_3^{2-}]^2} = \frac{(x)(x)}{(2.0 - 2x)^2} = \frac{x^2}{(2.0 - 2x)^2} = 2.\underline{4}65 \times 10^{-3}$$

Could assume "2x" is small compared to 2.0 since K is small.

However, don't have to since this is easy to solve. It's a perfect square so take the square root of both sides and get a first-order eqn. (linear eqn.). You should look for these kinds of things to make things easier to solve.

$$\frac{x}{(2.0 - 2x)} = 4.\underline{9}64 \times 10^{-2}$$

$$x = (4.\underline{9}64 \times 10^{-2})(2.0 - 2x)$$

$$x = (9.929 \times 10^{-2}) - (9.929 \times 10^{-2})x$$

$$(1.0992)x = (9.929 \times 10^{-2})$$

$$x = 9.\underline{0}3 \times 10^{-2}\text{ M} = \mathbf{9.0 \times 10^{-2}\ M}$$

If you did this by assuming the "2x" was small compared to 2.0 you would get:

$x =$ **9.9×10^{-2} M** (this was given as the answer assuming most everyone would do it this way and if done the other way the answer was closed enough for people to get the correct answer).