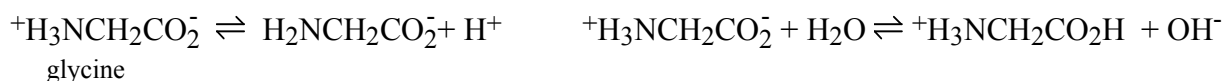


~~MONOPROTIC ACID-BASE EQUILIBRIA~~

S9-1. Write a charge balance for an aqueous solution of glycine, which reacts as follows:



S9-2. Write a charge balance for a solution of $\text{Al}(\text{OH})_3$ dissolved in 1 M KOH.

Possible species are Al^{3+} , AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})_4^-$.

S9-3. Write a mass balance for a 0.05 M solution of glycine (Problem S9-1) in water.

S9-4. Suppose that 0.30 g of AlOOH (FM 59.99) plus 150 mL of 3.0 M KOH are diluted to 1.00 L to give the same species produced by $\text{Al}(\text{OH})_3$ in Problem S9-2. Write mass balance equations for aluminum and potassium.

S9-5. Use the systematic treatment of equilibrium to calculate the concentration of Hg_2^{2+} in a saturated aqueous solution of $(\text{Hg}_2)_3[\text{Co}(\text{CN})_6]_2$ which dissociates into mercurous ion and $\text{Co}(\text{CN})_6^{3-}$ (cobalticyanide).

S9-6. A solution is prepared by mixing M_t moles of the salt MCl_2 (which dissociates completely to $\text{M}^{2+} + 2\text{Cl}^-$) and L_t moles of the ligand HL in 1 L. The following reactions may occur:



(a) Write a mass balance for the metal species.

(b) Write a mass balance for the ligand species. (c) Write a charge balance.

(d) Suppose that $M_t = L_t = 0.1$ M (exactly) and the pH is somehow fixed at 5.00.

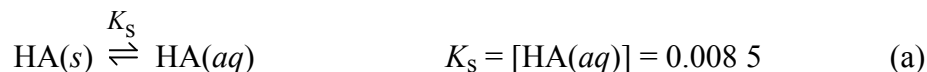
(This means that the charge balance no longer applies.) Use the equilibria and the two mass balances to find the concentrations of ML^+ , M^{2+} , L^- , and HL.

~~S9-7. (a) Use the procedure in Section 9-4 to find the concentrations of Mg^{2+} , F^- , and HF in a saturated aqueous solution of MgF_2 held at pH 3.00.~~

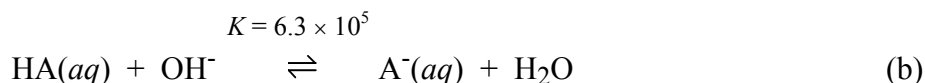
~~(b) Look up the formation constant for MgF^+ in the Appendix. Using the concentrations of Mg^{2+} and F^- from (a), calculate the concentration of MgF^+ . Is it negligible compared to $[\text{Mg}^{2+}]$? (The answer is no.)~~

~~(c) Because $[\text{MgF}^+]$ is not negligible compared to $[\text{Mg}^{2+}]$, we need to alter the mass balance to solve this problem correctly. Write the mass balance including the species MgF^+ .~~

S9-8. The acid HA has a solubility of 0.008 5 M in water at 25°C.

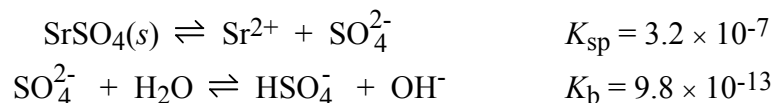


If NaOH is added to a suspension of solid HA in water, more acid dissolves because of the reaction



Consider a saturated solution, whose pH is somehow fixed at 10.00, in contact with excess solid HA. Calculate the total concentration of HA + A⁻.

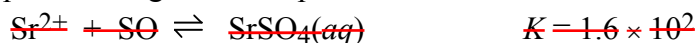
S9-9. Consider a saturated solution of SrSO₄ in which the following reactions can occur:



(a) Write mass and charge balances for this solution.

(b) Find the concentration of Sr²⁺ in the solution if the pH is fixed at 2.50.

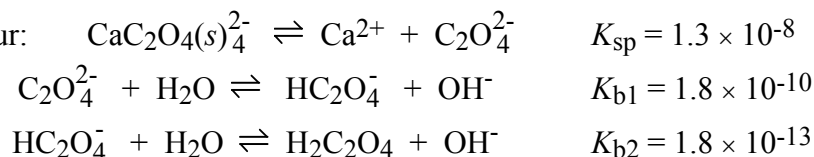
~~**S9-10.** The previous problem neglected ion pair formation:~~



~~(a) Write the mass balance including the ion pair.~~

~~(b) Find the concentrations of Sr²⁺ and SrSO₄(aq) if the pH is fixed at 2.50. What fraction of dissolved strontium is in the ion pair?~~

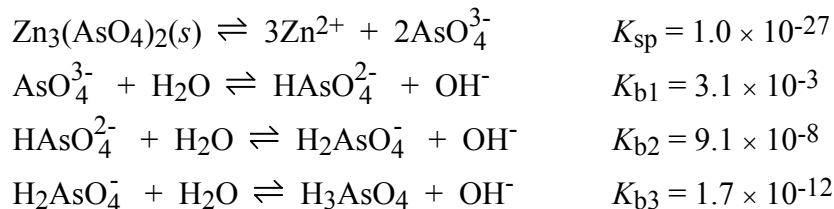
S9-11. Consider a saturated solution of calcium oxalate, CaC₂O₄, in which the following reactions can occur:



(a) Write mass and charge balances for this solution.


(b) Find the concentration of Ca²⁺ in the solution if the pH is fixed at 2.30.

S9-12. Consider a saturated solution of zinc arsenate, Zn₃(AsO₄)₂, in which the following reactions can occur:



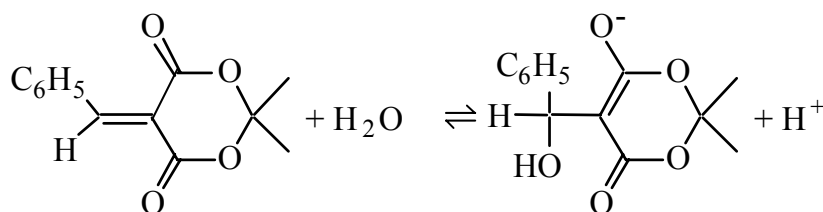
(a) Write mass and charge balances for this solution.

(b) Find the concentration of Zn²⁺ in the solution if the pH is fixed at 6.00.

~~**S9-13.**  Use the data in Problem S9-6 to construct a graph showing the concentrations of M²⁺, ML⁺, L⁻ and HL as a function of pH from 0 to 14 in 0.5 increments.~~

~~POLYPROTIC ACID-BASE EQUILIBRIA~~

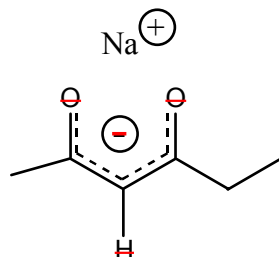
- S10-1.** Calculate the pH of (a) 5.0×10^{-4} M HNO_3 and (b) 5.0×10^{-4} M $(\text{CH}_3)_4\text{N}^+\text{OH}^-$.
- S10-2.** Calculate the pH of 2.0×10^{-7} M $(\text{CH}_3)_4\text{N}^+\text{OH}^-$.
What fraction of the total OH^- in this solution is derived from dissociation of water?
- ~~**S10-3.** Using activity coefficients correctly, calculate the pH of
(a) 0.050 M HBr (b) 0.050 M NaOH~~
- ~~**S10-4.** Using Appendix G, write structures of pyridine and pyridinium nitrate (pyridine-HNO_3).
Write the K_b reaction for pyridine and find the values of K_b and $\text{p}K_b$.~~
- S10-5.** Find the pH and fraction of dissociation (α) of a 0.0100 M solution of the weak acid HA with $K_a = 1.00 \times 10^{-4}$.
- S10-6.** Calculate the pH of 0.0850 M pyridinium bromide, $\text{C}_5\text{H}_5\text{NH}^+\text{Br}^-$.
- S10-7.** Find the pH and concentrations of cyclohexylamine ($\text{C}_6\text{H}_{11}\text{NH}_2$) and cyclohexylammonium ion ($\text{C}_6\text{H}_{11}\text{NH}_3^+$) in a 0.020 M solution of cyclohexylammonium iodide.
- ~~**S10-8.** A 0.100 M solution of the weak acid HA has a pH of 2.36. Calculate $\text{p}K_a$ for HA.~~
- ~~**S10-9.** (a) Calculate the pH and fraction of dissociation of $10^{-2.00}$ M hexane-2,4-dione.
(b) Calculate the pH and fraction of dissociation of $10^{-9.00}$ M hexane-2,4-dione.~~
- S10-10.** Compound A reacts with H_2O as follows:



The equilibrium constant (in aqueous methanol solution) is $10^{-5.4}$. Suppose that this same equilibrium constant applies in pure water. Find the pH of a 0.020 M solution of compound A.

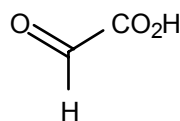
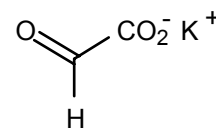
- S10-11.** Find the pH and fraction of association (α) of a 0.050 M solution of the weak base B with $K_b = 1.00 \times 10^{-4}$.
- S10-12.** Find the pH and concentrations of $(\text{CH}_3\text{CH}_2)_2\text{NH}$ and $(\text{CH}_3\text{CH}_2)_2\text{NH}_2^+$ in a 0.030 M solution of diethylamine.

- S10-13.** Find the pH and fraction of association (α) of 0.026 M NaOCl.
- S10-14.** Calculate the fraction of association (α) for 1.00×10^{-1} , 1.00×10^{-2} , and 1.00×10^{-12} M sodium formate.
- S10-15.** If a 0.030 M solution of a base has pH = 10.50, find K_b for the base.
- S10-16.** If a 0.030 M solution of a base is 0.27% hydrolyzed ($\alpha = 0.0027$), find K_b for the base.
- ~~**S10-17.** Calculate the pH and fraction of association of $10^{-2.00}$ M sodium hexane-2,4-dionate. (This salt is derived from the acid hexane-2,4-dione in Appendix G.)~~



sodium hexane-2,4-dionate

- S10-18.** Which buffer system will have the greatest buffer capacity at pH 8.5?
- (a) dimethylamine / dimethylammonium ion (c) hydroxylamine / hydroxylammonium ion
 (b) ammonia / ammonium ion (d) 3-nitrophenol / 3-nitrophenolate ion
- S10-19.** Find the pH of a solution prepared from 2.53 g of oxoacetic acid, 5.13 g of potassium oxoacetate and 103 g of water.

Oxoacetic acid
FM 74.036Potassium oxoacetate
FM 112.126

- S10-20.** Write the Henderson-Hasselbalch equation for a solution of methylamine. Calculate the quotient $[\text{CH}_3\text{NH}_2]/[\text{CH}_3\text{NH}_3^+]$ at (a) pH 4.00, (b) pH 10.64 and (c) pH 12.00.
- S10-21.** Given that pK_b for iodate ion IO_3^- is 13.83, find the quotient $[\text{HIO}_3]/[\text{IO}_3^-]$ in a solution of sodium iodate at (a) pH 7.00 and (b) pH 1.00.
- S10-22.** (a) Calculate the pH of a solution prepared by dissolving 10.0 g of tris(hydroxymethyl)aminomethane ("tris") plus 10.0 g of tris hydrochloride in 0.250 L of water.
 (b) What will be the pH if 10.5 mL of 0.500 M NaOH is added?
- S10-23.** How many milliliters of 0.113 M HBr should be added to 52.2 mL of 0.0134 M morpholine to give a pH of 8.00?

~~S10-24. (a) Calculate how many milliliters of 0.100 M HCl should be added to how many grams of sodium acetate dihydrate ($\text{NaOAc} \cdot 2\text{H}_2\text{O}$, FM 118.06) at 5°C to prepare 250.0 mL of 0.100 M buffer, pH 5.00. At 5°C, $\text{p}K_w = 14.734$ and $\text{p}K_a$ for acetic acid is 4.770.~~

~~(b) If you mixed what you calculated in part a, the pH would not be 5.00. Describe how you would actually prepare this buffer in the lab.~~

~~S10-25. Use Equations 10-20 and 10-21 to find the concentrations of B and BH^+ in a solution prepared by mixing 0.000 100 mol of propylamine plus 0.000 100 mol of propylammonium chloride in 1.00 L of water.~~

S10-26. (a) Use the systematic treatment of equilibrium (neglecting activity coefficients) to write all of the equations necessary to find $[\text{OH}^-]$ in a solution of a weak base, B, whose equilibrium constant is K_b and whose formal concentration is F. Combine the equations so that the only variable is $[\text{OH}^-]$ and rearrange your answer to the form


$$[\text{OH}^-]^3 + a[\text{OH}^-]^2 + b[\text{OH}^-] + c = 0.$$

(b) Use a spreadsheet to find the pH of 10^{-3} M B with $K_b = 10^{-5}$ and of 10^{-5} M B with $K_b = 10^{-9}$. You can solve the cubic polynomial by guessing values of $[\text{OH}^-]$ and having the spreadsheet evaluate the polynomial. When the polynomial is zero, you have guessed the correct value of $[\text{OH}^-]$.

~~S10-27. The temperature dependence of $\text{p}K_a$ for acetic acid is shown below. Is the dissociation of this acid endothermic or exothermic (a) at 5°C; (b) at 45°C?~~

°C	$\text{p}K_a$	°C	$\text{p}K_a$	°C	$\text{p}K_a$	°C	$\text{p}K_a$
0	4.781	15	4.758	30	4.757	45	4.777
5	4.770	20	4.756	35	4.762	50	4.787
10	4.762	25	4.756	40	4.769		

S10-28. Use the systematic treatment of equilibrium (neglecting activity coefficients) to write all the equations necessary to find the pH of a weak acid, HA. Combine the equations so that the only variable is $[\text{H}^+]$ and rearrange your answer to the form $[\text{H}^+]^3 + a[\text{H}^+]^2 + b[\text{H}^+] + c = 0$.

S10-29.  Use the equation from the previous problem to find the pH of a 1.00×10^{-4} M solution of acid with $\text{p}K_a = 4.00$. To find the pH, guess values of pH and use a spreadsheet to evaluate the polynomial. When you have guessed the right pH, the polynomial will be 0.

~~S10-30. Use the systematic treatment of equilibrium (with activity coefficients) to write all the equations necessary to find the pH of a weak acid, HA. Combine the equations so that the only variable is $[\text{H}^+]$ and rearrange your answer to the form $[\text{H}^+]^3 + a[\text{H}^+]^2 + b[\text{H}^+] + c = 0$.~~

~~ACID-BASE TITRATIONS~~

- S11-1.** Write the chemical reactions whose equilibrium constants are K_{b1} and K_{b2} for the amino acid serine. Find the values of K_{b1} and K_{b2} .
- S11-2.** Consider the diprotic acid H_2A with $K_1 = 1.00 \times 10^{-5}$ and $K_2 = 1.00 \times 10^{-9}$. Find the pH and concentrations of H_2A , HA^- , and A^{2-} in the following solutions: (a) 0.100 M H_2A , (b) 0.100 M $NaHA$, and (c) 0.100 M Na_2A .
- ~~**S11-3.** Find the pH of 0.150 M piperazine monohydrochloride, piperazine \cdot HCl. Calculate the concentration of each form of piperazine in this solution.~~
- ~~**S11-4.** Write down, but do not attempt to solve, the exact equations needed to calculate the composition of one liter of solution containing F_1 mol of HCl, F_2 mol of disodium ascorbate (Na_2A , the salt of a weak acid whose two K_a values may be called K_1 and K_2), and F_3 mol of trimethylamine (a weak base, B, whose equilibrium constant should be called K_b). Include activity coefficients wherever appropriate.~~
- S11-5.** How many mL of 0.423 M KOH should be added to 5.00 g of tartaric acid (2,3-dihydroxybutanedioic acid, FM 150.08) before diluting to 50 mL to give a buffer of (a) pH 3.00 and (b) pH 4.00?
- S11-6.** How many mL of 0.421 M HCl should be added to 50.0 mL of 0.055 5 M disodium malonate ($NaO_2CCH_2CO_2Na$, FM 148.03, the salt of malonic acid) to adjust the pH to (a) 6.00 and (b) 3.20?
- S11-7.** How many grams of oxalic acid (FM 90.04) should be mixed with 5.00 g of $K_2C_2O_4$ (FM 166.22) to give a pH of 3.20 when diluted to 250 mL?
- ~~**S11-8.** Starting with the fully protonated species, write the stepwise acid dissociation reactions of the amino acids aspartic acid and arginine. Be sure to remove the protons in the correct order. Which species are the neutral molecules that we call aspartic acid and arginine?~~
- ~~**S11-9.** (a) Find the quotient $[H_2His^+]/[HHis]$ in a 0.050 0 M histidine solution.
(b) Find the same quotient for 0.050 0 M histidine monohydrochloride ($His \cdot HCl$).~~
- ~~**S11-10.** Find the pH and concentration of each species of arginine in 0.012 0 M arginine-HCl solution.~~
- S11-11.** Consider the neutral base pyrrolidine, C_4H_9N , designated B.
(a) Which is the predominant species, B or BH^+ , at pH 11? at pH 12?

(b) At what pH is $[BH^+] = [B]$?

(c) What is the quotient $[B]/[BH^+]$ at pH 12.00? at pH 2.00?

S11-12. Which is the predominant form of sulfurous acid at pH (a) 2, (b) 4, (c) 6 and (d) 8?

~~S11-13.~~ What is the charge of the predominant form of citric acid at pH 5.00?

~~S11-14.~~ The acid HA has $pK_a = 7.00$. Use Equations 11-17 and 11-18 to find the fraction in the form HA and the fraction in the form A^- at pH = 8.00. Does your answer agree with what you expect for the quotient $[A^-]/[HA]$ at pH 8.00?

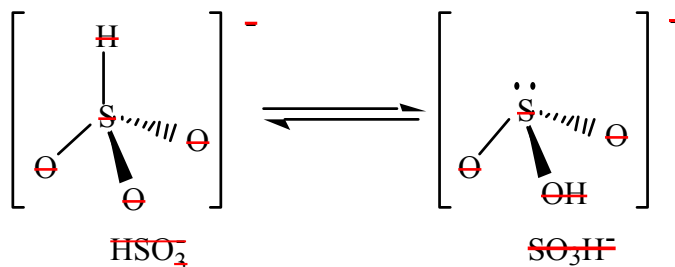
~~S11-15.~~ A dibasic compound, B, has $pK_{b1} = 2.00$ and $pK_{b2} = 8.00$. Find the fraction in the form BH_2^{2+} at pH 9.00 using Equation 11-19. Note that K_1 and K_2 in Equation 11-19 are acid dissociation constants for BH_2^{2+} ($K_1 = K_w/K_{b2}$ and $K_2 = K_w/K_{b1}$):

~~S11-16.~~ What fraction of 1,6-hexanedioic acid (adipic acid) is in each form (H_2A , HA^- , A^{2-}) at pH 5.00? at pH 6.00?

~~S11-17.~~ Calculate α_{H_2A} , α_{HA^-} , and $\alpha_{A^{2-}}$ for butane-2,3-dione dioxime (dimethylglyoxime) at pH 10.00, 10.66, 11.00, 12.00, and 12.50.

~~S11-18.~~ Calculate the isoelectric and isoionic pH of 0.010 M 8-hydroxyquinoline.

~~S11-19.~~ *Thermodynamics and propagation of uncertainty.* The bisulfite ion exists in the following equilibrium forms:



The temperature dependence of the equilibrium constant at an ionic strength of 1.0 M is $\ln K = 3.23 (\pm 0.53) + 1.44 (\pm 0.15) \times 10^3 \times (1/T)$, where T is temperature in kelvins. Because $\ln K$ must be dimensionless, the number 3.23 is dimensionless and the number 1.44×10^3 has the unit of kelvins.

(a) Using Equation 6-8, calculate the enthalpy change, ΔH° , and the entropy change, ΔS° , for the isomerization reaction. Include uncertainties in your answers.

(b) Calculate the quotient $[SO_3H^-]/[HSO_3^-]$ at 298 K, including estimated uncertainty.

- ~~S12-1. Consider the titration of 25.0 mL of 0.050 0 M HClO_4 with 0.100 M KOH. Find the pH at the following volumes of base added and make a graph of pH versus V_b : $V_b = 0, 1, 5, 10, 12.4, 12.5, 12.6$ and 13 mL.~~
- ~~S12-2. A volume of 50.0 mL of 0.050 0 M weak acid HA ($\text{p}K_a = 4.00$) was titrated with 0.500 M $[\text{CH}_3]_4\text{N}^+\text{OH}^-$ (tetramethylammonium hydroxide, a strong base). Find the pH at the following volumes of base added and make a graph of pH versus V_b : $V_b = 0, 1, 2.5, 4, 4.9, 5, 5.1,$ and 6 mL.~~
- ~~S12-3. Using the same instructions as Problem 12-7, sketch the titration curve for the reaction of 50.0 mL of 0.050 0 M 4-nitrophenol with 0.100 M NaOH.~~
- S12-4. When 16.24 mL of 0.064 3 M KOH was added to 25.00 mL of 0.093 8 M weak acid, HA, the observed pH was 3.62. Find $\text{p}K_a$ for the acid.
- ~~S12-5. A 50.0 mL aliquot of 0.050 M weak base B ($\text{p}K_b = 4.00$) was titrated with 0.500 M HNO_3 . Find the pH at the following volumes of acid added and make a graph of pH versus V_a : $V_a = 0, 1, 2.5, 4, 4.9, 5, 5.1,$ and 6 mL.~~
- ~~S12-6. A solution of 100.00 mL of 0.040 0 M sodium propanoate (the sodium salt of propanoic acid) was titrated with 0.083 7 M HCl. Calculate the pH at the points $V_a = 0, \frac{1}{4} V_e, \frac{1}{2} V_e, \frac{3}{4} V_e, V_e,$ and $1.1 V_e$.~~
- ~~S12-7. A volume of 50.0 mL of the dibasic compound B (0.050 0 M, $\text{p}K_{b1} = 5.00, \text{p}K_{b2} = 9.00$) was titrated with 0.500 M HCl. Find the pH at the following volumes of acid added and make a graph of pH versus V_a : $V_a = 0, 1, 2.5, 4, 4.8, 5, 5.2, 6, 7.5, 9, 9.8, 10, 10.2, 11$ and 12 mL.~~
- ~~S12-8. A 50.0 mL aliquot of 0.050 0 M diprotic acid H_2A ($\text{p}K_1 = 5.00, \text{p}K_2 = 9.00$) was titrated with 0.500 M NaOH. Find the pH at the following volumes of base added and make a graph of pH versus V_b : $V_b = 0, 1, 2.5, 4, 4.8, 5, 5.2, 6, 7.5, 9, 9.8, 10, 10.2, 11$ and 12 mL.~~
- ~~S12-9. Calculate the pH at 2 mL intervals (from 0 to 12 mL) in the titration of 25.0 mL of 0.100 M cyclohexylamine with 0.250 M HI. Make a graph of pH versus V_a .~~
- S12-10. A solution containing 0.010 0 M tyrosine was titrated to the first equivalence point with 0.004 00 M KOH.
- (a) Draw the structures of reactants and products.

~~(b) Calculate the pH at the first equivalence point.~~

S12-11. How many milliliters of 0.0431 M NaOH should be added to 59.6 mL of 0.122 M leucine to obtain a pH of 8.00?

~~**S12-12.** Consider the neutral form of the amino acid histidine, which we will abbreviate HA.~~

~~(a) Write the sequence of reactions that occurs when HA is titrated with HClO₄. Draw structures of reactants and products.~~

~~(b) How many mL of 0.0500 M HClO₄ should be added to 25.0 mL of 0.0400 M HA to give a pH of 3.00?~~

~~**S12-13.** What color change would you expect to see during the upper titration in Figure 12-4 with bromothymol blue indicator?~~

~~**S12-14.** Cresol purple has two transition ranges listed in Table 12-4. What color would you expect it to be at the following pH values? (a) 1 (b) 3 (c) 7 (d) 10~~

~~**S12-15.** Why would an indicator end point not be very useful in the titration curve for pK_a = 10.00 in Figure 12-3?~~

~~**S12-16.** Consider the titration of 0.10 M pyridinium bromide (the salt of pyridine plus HBr) by 0.10 M NaOH. Sketch the titration curve using calculated pH values for the volumes 0.99 V_e, V_e, and 1.01 V_e. Select an indicator from Table 12-4 that would be suitable for this titration and state what color change will be used.~~

~~**S12-17.** A very weak basic aromatic amine (pK_b = 14.79) was used to measure the pH of a concentrated acid. A solution was prepared by dissolving 6.390 mg of the amine (FM 278.16) in 100.0 mL of the acid. The absorbance measured at 385 nm in a 1.000-cm cell was 0.350. Find the pH of the solution~~



~~**S12-18.** An aqueous solution containing 1 g of oxobutanedioic acid (FM 132.073) per 100 mL was titrated with 0.09432 M NaOH to measure the acid molarity.~~

~~(a) What will be the pH at each equivalence point?~~

~~(b) Which equivalence point would be best to use in this titration?~~

~~(c) You have the indicators erythrosine, ethyl orange, bromocresol green, bromothymol blue, thymolphthalein, and alizarin yellow. Which indicator will you use and what color change will you look for?~~

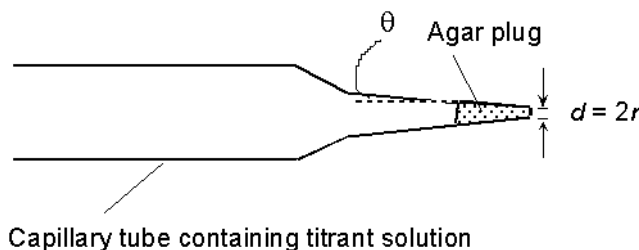
~~S12-19. Borax (Table 12-5) was used to standardize a solution of HNO_3 . Titration of 0.2619 g of borax required 21.61 mL. What is the molarity of the HNO_3 ?~~

~~S12-20. Derive the equation in Table 12-6 for titrating dibasic B with strong acid.~~

~~S12-21. Activity coefficients in titration equations. In the titration of a weak acid by a strong base, activity coefficients do not enter the charge or mass balances and therefore do not appear in Equation 12-9. In a rigorous treatment, the only way activity coefficients enter any of the equations in Table 12-6 is in the fractional composition equations. Using activity coefficients correctly, derive the following expressions for α_{HA} and α_{A^-} . These are the expressions that should be used with Equation 12-9 in a rigorous treatment of a titration.~~

$$\alpha_{\text{HA}} = \frac{[\text{H}^+]^{\gamma_{\text{H}^+}\gamma_{\text{A}^-}}}{[\text{H}^+]^{\gamma_{\text{H}^+}\gamma_{\text{A}^-}} + K_a^{\gamma_{\text{HA}}}} \quad \alpha_{\text{A}^-} = \frac{K_a^{\gamma_{\text{HA}}}}{[\text{H}^+]^{\gamma_{\text{H}^+}\gamma_{\text{A}^-}} + K_a^{\gamma_{\text{HA}}}}$$

~~S12-22. Diffusional microburet. A capillary tube drawn to a fine point and containing a porous plug at the outlet delivers titrant at a tiny, well-defined rate. For the capillary shown, the rate of delivery of titrant is~~



$$\text{rate (mol/s)} = D_m [T] r \tan \theta$$

~~where D_m is the diffusion coefficient of reagent in the capillary plug (which is nearly the same as the diffusion coefficient in free solution), $[T]$ is the concentration of titrant in the capillary, r is the radius of the opening of the capillary (= half of the diameter, d), and θ is the cone angle defined in the diagram. For KOH titrant, the diffusion coefficient is $2.0 \times 10^{-9} \text{ m}^2/\text{s}$. Find the delivery rate (fmol/s) for 0.020 M KOH from a microburet with $r = 0.40 \text{ } \mu\text{m}$ and $\theta = 3.0^\circ$. Express the rate of delivery of titrant from this buret in microliters per year.~~