

Chem 332
Analytical Chemistry
Exam I

Name:

Show all work for partial credit

1. (10 points) How many milliliters of 0.113M HBr should be added to 52.2 ml of 0.0134 M morpholine to give a pH of 8? (The pK_a of morpholine is 8.492)

From the assigned problems!

$$pH = pK_a + \log A^-/HA$$

$$8 = 8.492 + \log A^-/HA$$

$$-.492 = \log A^-/HA$$

$$10^{-.492} = \log A^-/HA$$

$$.322 = A^-/HA$$

52.2 ml of .0134M morpholine = .699 mmoles

The trick here is that morpholine is a base, so it goes in the A^- portion

The HBr will protonate it into the acid form thus we have:

$$.322 = .699 - X/X; .332X = .699 - X; 1.332X = .699; X = .525 \text{ mmoles}$$

$$.113M = .525 \text{ mmoles}/X; \quad \mathbf{X = 4.6 \text{ ml}}$$

2A. (10 points) Hydroxylamine is a base and has a chemical formula of $HONH_2$ and a K_a of 1.1×10^{-6}

What is the pH of a .1M solution of hydroxylamine hydrochloride $HONH_3Cl$?

What is the pH of a .1M solution of hydroxylamine $HONH_2$?

What is the pH of a solution that is .05M $HONH_3Cl$ and .05 M $HONH_2$?

If hydroxylamine is a base, then hydroxylamine hydrochloride, is the protonated, or acid form, so you use the weak acid for and the K_a .

$$1.1 \times 10^{-6} = X^2/.1 - X$$

K_a is small so we can assume

$$1.1 \times 10^{-6} \approx X^2/.1$$

$$X = \sqrt{1.1 \times 10^{-7}}$$

$$X = 3.32 \times 10^{-4}; \quad \mathbf{pH = 3.48}$$

Hydroxylamine itself is a base so you use the weak base equation, but you need to convert K_a into K_b

$$K_w = K_a \times K_b; \quad K_b = K_w/K_a; \quad K_b = 1 \times 10^{-14}/1.1 \times 10^{-6} = 9.09 \times 10^{-9}$$

$$9.09 \times 10^{-9} = X^2/.1 - X \text{ Again } K \text{ is small so we can assume}$$

$$9.09 \times 10^{-9} \approx X^2/.1$$

$$X = \sqrt{9.09 \times 10^{-10}}; \quad X = 3.02 \times 10^{-5}, \quad pOH = -4.52; \quad \mathbf{pH = 9.48}$$

A mixture of equal moles of acid and base would be a buffer with $pH = pK_a + \log(.1/.1); \quad pH = pK_a; \quad = -\log(1.1 \times 10^{-6}) = \mathbf{5.96}$

2B.1 (2 points) Make a rough sketch of the titration of .1M hydroxylamine hydrochloride with .1M NaOH. (No further calculations are needed, ignore dilution effects))

Rough sketches are hard on a computer, so I will describe the curve. This would be the acid form being titrated until it is converted to a base, so the pH would start at the pH given for hydroxylamine hydrochloride (3.48), there would be a buffer region at pH 5.96, and the equivalence point would have a pH of 9.48

2B.2 (3 points) What indicator would you use for this titration, methyl orange with a transition range of 3.1-4.4, thymolphthalein with a transition range of 8.3-10.5 or phenol red with a transition range of 6.4-8.0?

The best match with the equivalence point is thymolphthalein

2C.1 (2 points) Make a rough sketch of the titration of .1M hydroxylamine with .1M HCl (No further calculations are needed, ignore dilution effects)

Rough sketches are hard on a computer, so I will describe the curve. This would be the Base form being titrated until it is converted to a base, so the pH would start at the pH 9.48, there would be a buffer region at pH 5.96, and the equivalence point would have a pH of 3.48

2C.2 (3 points) What indicator would you use for this titration, methyl orange with a transition range of 3.1-4.4, thymolphthalein with a transition range of 8.3-10.5 or phenol red with a transition range of 6.4-8.0?

The best match with the equivalence point is methyl orange

3. (10 points) The primary standard, KHP we used in the lab to standardize our NaOH is derived from the chemical phthalic acid, which is a diprotic acid with K_a 's of 1.2×10^{-3} and 3.9×10^{-5} . As a diprotic acid it can exist in three different forms as H_2A , HA^- , and A^{2-} . In what range of pH's is H_2A the predominate form found in solution? In what range of pH's is HA^- the predominate form found in solution? In what range of pH's is A^{2-} the predominate form found in solution?

The fully protonated H_2A form will predominate at all pH's < than $pK_{A1} = 2.89$

The HA^- will predominate from 2.89 until $pK_{A2} = 4.4$

And the A^{2-} form will predominate at pH's > 4.4

4. (10 points) What is the ionic strength of a solution that is 1M KCl and .05M $Ni(NO_3)_4$

$$\begin{aligned}\mu &= 1/2([K^+]1^2 + [Cl^-](-1)^2 + [Ni^{+4}](+4)^2 + [NO_3^-](-1)^2) \\ \mu &= 1/2([1]1 + 1 + [.05](16) + [.2](1)) \\ \mu &= 1.5\end{aligned}$$

5. (10 points) Given that the K_f for the V^{2+} -EDTA complex is 5×10^{12} , would a titration performed at pH 7 be considered feasible? (The α_{Y-4} for EDTA at pH 7 is 5×10^{-4})

$$K_{\text{eff}} = 5 \times 10^{12} \times 5 \times 10^{-4} = 25 \times 10^8 = 2.5 \times 10^9$$

$K_{\text{eff}} > 1 \times 10^8$, so the titration would be feasible

Take home

6A (5 points) Dichloroacetic acid (Cl_2CHCO_2H) has a K_a of 8×10^{-2} . What is the pH of a .1M solution of Dichloroacetic acid, ignoring all activity effects.

$$8 \times 10^{-2} = X^2 / .1 - X$$

K_A is so large that this must be solved exactly

Using successive approximation takes 15 iterations or more, so this is easier to use the solver or the quadratic and you get

$$X = [H^+] = .058; \text{pH} = 1.24$$

6B. (10 points) Now recalculate the pH of this solution including all activity effects.

$$[H^+] = .058, [A^-] = .058, \text{ so } \mu = .058$$

$$\log \gamma_{H^+} = -.51 (+1)^2 \text{sqrt}(.058) / [1 + 900 \text{sqrt}(.058) / 305]$$
$$= -.072$$

$$\gamma_{H^+} = .848$$

$$\log \gamma_{A^-} = -.51 (+1)^2 \text{sqrt}(.058) / [1 + 500 \text{sqrt}(.058) / 305]$$
$$= -.085$$

$$\gamma_{A^-} = .816$$

$$8 \times 10^{-2} = .848[H^+].816[A^-] / .1 - [A^-]$$
$$= .848 \times .816 \times (X) / (.1 - X)$$

solving with quadratic

$$X = [H^+] = .064$$

It you wanted to solve this exactly you would now recalculate μ and iterate a few times!

$$\text{pH} = -\log(\gamma[H^+])$$
$$= -\log(.848 \times .064)$$
$$= 1.26$$

6C (10 points) Now calculate the pH of this solution if Na_2SO_4 is added to the solution to give it a final concentration of .1M Na_2SO_4 .

$$\begin{aligned}\mu &= 1/2([\text{H}^+](1)^2 + [\text{A}^-](-1)^2 + [\text{Na}^+](1)^2 + [\text{SO}_4^{2-}](-2)^2) \\ &= 1/2(.064 + .064 + .2 + .1(4)) \\ &= .364\end{aligned}$$

Note: this is technically too large to properly use the Debye equations!

$$\begin{aligned}\log \gamma_{\text{H}^+} &= -.51 (+1)^2 \sqrt{.364} / [1 + 900 \sqrt{.364} / 305] \\ &= -.111\end{aligned}$$

$$\gamma_{\text{H}^+} = .775$$

$$\begin{aligned}\log \gamma_{\text{A}^-} &= -.51 (+1)^2 \sqrt{.364} / [1 + 500 \sqrt{.064} / 305] \\ &= -.155\end{aligned}$$

$$\gamma_{\text{A}^-} = .700$$

$$\begin{aligned}8 \times 10^{-2} &= .775[\text{H}^+].700[\text{A}^-] / .1 - [\text{A}^-] \\ &= .848x.816x(X) / (.1 - X) \\ &\text{solving with quadratic} \\ X = [\text{H}^+] &= .0683\end{aligned}$$

If you wanted to solve this exactly you would now recalculate μ and iterate a few times!

$$\begin{aligned}\text{pH} &= -\log(\gamma[\text{H}^+]) \\ &= -\log(.775 \times .0683) \\ &= \mathbf{1.28}\end{aligned}$$

7. (10 points) I would like to titrate 25 ml of 0.02 M Fe^{3+} with 0.019M EDTA in a solution buffered at pH 10. What is the pFe^{3+} in the following 4 points of the titration curve: (A) Initial point, (B) $\frac{1}{2}$ way between initial point and equivalence point, (C) equivalence point, (D) 1 ml after the equivalence point.

$$\begin{aligned}25 \text{ ml} \times .02 \text{ M} &= .5 \text{ mmoles } \text{Fe}^{3+} = 0.5 \text{ mmole EDTA at equivalence point} \\ .019\text{M EDTA} &= 0.5 \text{ mmoles}/X ; X = 26.32 \text{ ml}\end{aligned}$$

So points are 0, 13.16, 26.32, and 27.32 ml

0

$$\text{pFe} = -\log(.02) = \mathbf{1.70}$$

13.16

$$\begin{aligned}\text{mmole Fe} &= .5 \\ \text{mmoles EDTA} &= .019 \times 13.16 = .25 \text{ mmole} \\ \text{mmoles Fe in solution} &= .25 \\ [\text{Fe}^{3+}] &= .25 / (25 + 13.16) = .00655; \quad \mathbf{pFe = 2.18}\end{aligned}$$

26.32

$$\begin{aligned}\text{mmoles Fe} &= .5 \\ \text{mmoles EDTA} &= .5\end{aligned}$$

After reaction we have .5 mmole Fe·EDTA
[Fe·EDTA]=.5/(25+26.32) = .00974

$$K_{\text{eff}} = 1.259 \times 10^{25} \times .3 \\ = 3.78 \times 10^{24}$$

$$3.78 \times 10^{24} = .00974 / X^2; X^2 = .00974 / 3.78 \times 10^{24} \\ X = 5.08 \times 10^{-14}; \text{pFe} = 13.29$$

27.32 ml

$$[\text{Fe} \cdot \text{EDTA}] = 5 \text{ mmoles} / (25 + 27.32) = .00956 \\ [\text{EDTA}]_{\text{excess}} = (1 \text{ ml} \times .019 \text{ M}) / (25 + 27.32) = .000363 \\ 3.78 \times 10^{24} = .00956 / (.000363 X); X = .00956 / (3.78 \times 10^{24} \times .000363) \\ X = 6.97 \times 10^{-24}; \text{pFe} = 23.16$$

8A (5 points) I am going to mix 1 ml of 1M Ca(NO₃)₂ with 2 mls of .5M MgCl₂, 3 mls of 0.25M Na₂CO₃ and 1 ml of 0.25 M H₂CO₃. I think a lot of chemistry might occur. The CO₃²⁻ ion should try to precipitate with both Ca²⁺ and Mg²⁺, as well as neutralize the some of the H₂CO₃.

List all chemical species in this solution, and then try to come up with enough chemical equations to solve the system.

8B (Bonus points) You get two bonus points for each concentration in 8A that you solve for correctly! (Including the obvious ones)

Species in solution



Species precipitating?



11 aqueous species, 2 precipitating species

Equations:

$$4.46 \times 10^{-7} = [\text{H}^+][\text{HCO}_3^-] / [\text{H}_2\text{CO}_3]$$

$$4.69 \times 10^{-11} = [\text{H}^+][\text{CO}_3^{2-}] / [\text{HCO}_3^-]$$

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$4.5 \times 10^{-9} = [\text{Ca}^{2+}][\text{CO}_3^{2-}]$$

$$3.5 \times 10^{-8} = [\text{Mg}^{2+}][\text{CO}_3^{2-}]$$

$$\text{Charge Balance: } [\text{H}^+] + [\text{Na}^+] + 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] = [\text{OH}^-] + [\text{NO}_3^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$$

Mass Balance eqns:

$$[\text{NO}_3^-] = (1 \text{ M} \times 1 \text{ ml} \times 2) / 7 \text{ ml}$$

$$[\text{Cl}^-] = (.5 \text{ M} \times 2 \text{ ml} \times 2) / 7 \text{ ml}$$

$$[\text{Na}^+] = (.25 \text{ M} \times 3 \text{ ml} \times 2) / 7 \text{ ml}$$

$$[\text{Ca}^{2+}] = (1 \text{ M} \times 1 \text{ ml} \times 1) / 7 \text{ ml} \text{ If and only if no precipitate forms}$$

$$[\text{Mg}^{2+}] = (.5 \text{ M} \times 2 \text{ ml} \times 1) / 7 \text{ ml} \text{ If and only if no precipitate forms}$$

$$[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = [(.25 \text{ M} \times 3 \text{ ml} \times 1) + (.25 \text{ M} \times 1 \text{ ml} \times 1)] / 7 \text{ ml}$$

If an only if no precipitate forms

12 equations, 11 unknowns, should be solvable if no precipitate forms
If ppt forms its going to be interesting

8B actual concentrations (bonus points)

$$[\text{H}_2\text{O}] = 1/.018 = 55.5\text{M} \text{ I said +2 points even for the obvious ones!}$$

$$[\text{NO}_3^-] = .286 \text{ M}$$

$$[\text{Cl}^-] = .286 \text{ M}$$

$$[\text{Na}^+] = .214 \text{ M}$$

$$[\text{Ca}^{2+}]^* = .142\text{M}$$

$$[\text{Mg}^{2+}]^* = .142\text{M}$$

$$\text{Total carbonate } * = (.75 + .25)/7 = .142\text{M}$$

Trial assumptions



The reaction of a weak base and a weak acid. Never did this before, does this make sense?

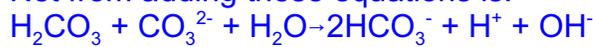
Weak acid



Weak base

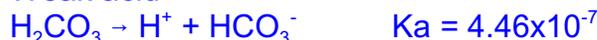


Net from adding these equations is:



To get rid of H^+ and OH^- products we need 1 more reaction

Weak acid



Weak base



Reverse of K_w



Net now



$$K = 9,500$$

Not a great K, but enough to show that re reaction will go forward

If above is true

$$\text{Mole } \text{H}_2\text{CO}_3 = .25 \text{ mmole}$$

$$\text{Mole } \text{CO}_3^{2-} = .75 \text{ mmole}$$

RXN table

	H_2CO_3	+	CO_3^{2-}	\rightarrow	2HCO_3^-
	.25		.75		
	-.25		-.25		+.5
Net	0		.5		.5

after reaction

$$\text{pH} = \text{pKa}_2 + \log(.5/.5)$$

$$= 10.33$$

Now the interesting calculation

$$[\text{CO}_3^{2-}] = .5 \text{ mmole} / 7 \text{ ml} = .0714 \text{ M}$$

Plug this into the K_{sp} with [Mg] and [Ca]

if ppt forms, then this may be difficult to solve

if ppt doesn't form we solve for everything.

$$Q_{\text{MgCO}_3} = .0714 \times .142 = .010$$

$$K_{\text{SP MgCO}_3} = 5 \times 10^{-8}$$

Q > K Too many products, ppt will form

$$Q_{\text{CaCO}_3} = .0714 \times .142 = .01$$

$$K_{\text{SP CaCO}_3} = 4.5 \times 10^{-9}$$

Q > K Too many products, ppt will form

As ppt forms, CO_3^{2-} is pulled from solution, pH shifts, HCO_3^- changes to CO_3^{2-} and everything goes to H— in a handbasket as far as our calculations are concerned.