Show all work for partial credit

1. (10 points) 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? (The pKₐ of morpholine is 8.492)

From the assigned problems!

\[ \text{pH} = \text{pK}_a + \log \frac{A}{HA} \]

\[ 8 = 8.492 + \log \frac{A}{HA} \]

\[ -.492 = \log \frac{A}{HA} \]

\[ 10^{-0.492} = \log \frac{A}{HA} \]

\[ .322 = \log \frac{A}{HA} \]

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:

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

\[ .113M = .525 \text{ mmoles} / X; X = 4.6 \text{ ml} \]

2A. (10 points) Hydroxylamine is a base and has a chemical formula of HONH₂ and a Kₐ of 1.1x10⁻⁶

What is the pH of a .1M solution of hydroxylamine hydrochloride HONH₃Cl?

What is the pH of a .1M solution of hydroxylamine HONH₂?

What is the pH of a solution that is .05M HONH₃Cl and .05 M HONH₂?

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

\[ 1.1 \times 10^{-6} = X^2 / 1 - X \]

\[ K_a \text{ is small so we can assume} \]

\[ 1.1 \times 10^{-5} = X^2 / 1 \]

\[ X = \sqrt{(1.1 \times 10^{-7})} \]

\[ X = 3.32 \times 10^{-4}; \text{ pH} = 3.48 \]

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

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

\[ 9.09 \times 10^{-9} = X^2 / 1 - X \]

Again K is small so we can assume

\[ 9.09 \times 10^{-9} = X^2 / 1 \]

\[ X = \sqrt{(9.09 \times 10^{-10})}; X = 3.02 \times 10^{-5}, \text{ pOH} = -4.52; \text{ pH} = 9.48 \]

A mixture of equal moles of acid and base would be a buffer with

\[ \text{pH} = \text{pK}_a + \log(.1 / .1); \text{ pH} = \text{pK}_a; = \log(1.1 \times 10^{-5}) = 5.96 \]
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 Ka's of 1.2x10\(^{-3}\) and 3.9x10\(^{-5}\). As a diprotic acid it can exist in three different forms as H\(_2\)A, HA\(^-\), and A\(^{2-}\).

In what range of pH's is H\(_2\)A 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\(_2\)A 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\(_3\))\(_4\)

\[ \mu = \frac{1}{2} \left( [K^+]^2 + [Cl^-]^2 + [Ni^{4+}]^2 + [NO_3^-]^2 \right) \]
\[ \mu = \frac{1}{2} \left( [1]^2 + [1]^2 + [.05]^2 \right) \]
\[ \mu = 1.5 \]
5. (10 points) Given that the $K_e$ for the $V^{2+}$-EDTA complex is $5 \times 10^{12}$, would a titration performed at pH 7 be considered feasible? (The $\alpha_{Y^4}$ for EDTA at pH 7 is $5 \times 10^{-4}$)

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

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

**Take home**

6A (5 points) Dichloroacetic acid ($\text{Cl}_2\text{CHCO}_2\text{H}$) has a $K_a$ of $8 \times 10^{-2}$. What is the pH of a .1M solution of Dichloroacetic acid, ignoring all activity effects.

\[ 8 \times 10^{-2} = \frac{X^2}{1-X} \]

$K_a$ 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.

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

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

\[ \gamma_{H^+} = .848 \]

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

\[ \gamma_{A^-} = .816 \]

\[ 8 \times 10^{-2} = 0.848[H^+]0.816[A^-]/[1-[A^-]] \]

\[ = 0.848 \times 0.816 \times (X)/(1-X) \]

solving with quadratic

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

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

\[ \text{pH} = -\log(\gamma[H^+]) \]

\[ = -\log(0.848 \times 0.064) \]

\[ = 1.26 \]
6C (10 points) Now calculate the pH of this solution if Na$_2$SO$_4$ is added to the solution to give it a final concentration of .1M Na$_2$SO$_4$.

\[
\mu = \frac{1}{2}(\text{[H}^+\text{]}(1)^2 + \text{[A}^-\text{]}(-1)^2 + \text{[Na}^+\text{]}(1)^2 + \text{[SO}_4^{2-}\text{]}(-2)^2)
\]
\[
= \frac{1}{2}(0.064 + 0.064 + 0.2 + 0.1(4))
\]= 0.364

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

\[
\log_{Y_{H^+}} = -0.51 + (1)^2 \sqrt{0.364}/[1 + 900 \sqrt{0.364}/305]
\]
\[
= -0.111
\]

\[
Y_{H^+} = 0.775
\]

\[
\log_{Y_{A^-}} = -0.51 - \sqrt{0.364}/[1 + 500 \sqrt{0.064}/305]
\]
\[
= -0.155
\]

\[
Y_{A^-} = 0.700
\]

8x10^{-2} = 0.775[H^+].700[A^-]/.1-[A^-]
\[
=.848x.816x(X)/(1-X)
\]
solving with quadratic
\[
X = [H^+] = 0.0683
\]

It you wanted to solve this exactly you would now recalculate \(\mu\) and iterate a few times!

\[
\text{pH} = -\log(y[H^+])
\]
\[
= -\log(0.775 \times 0.0683)
\]
\[
= 1.28
\]

7. (10 points) I would like to titrate 25 mls of 0.02 M Fe$^{3+}$ with 0.019M EDTA in a solution buffered at pH 10. What it the pFe$^{3+}$ in the following 4 points of the titration curve: (A) Initial point, (B) ½ way between initial point and equivalence point, (C) equivalence point, (D) 1 ml after the equivalence point.

25 ml x .02 M = .5 mmoles Fe$^{3+}$ = 0.5 mmole EDTA at equivalence point

.019M EDTA = 0.5 mmoles/X ; X = 26.32 ml

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

0
pFe =-log(.02) = 1.70

13.16

mmole Fe = .5

mmoles EDTA = .019 x 13.16 = .25 mmole

mmoles Fe in solution = .25

[Fe$^{3+}$] = .25/(25+13.16) = .00655; \(pFe = 2.18\)

26.32

mmoles Fe=.5

mmoles EDTA = .5
After reaction we have .5 mmole Fe-EDTA

\[ [\text{Fe-EDTA}] = \frac{.5}{(25+26.32)} = .00974 \]

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

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

27.32 ml

\[ [\text{Fe-EDTA}] = \frac{5 \text{ mmoles}}{(25+27.32)} = .00956 \]
\[ [\text{EDTA}] \text{ excess} = \frac{1 \text{ ml} \times .019 \text{ M}}{(25+27.32)} = .000363 \]
\[ 3.78 \times 10^{24} = .00956/0.000363X; \quad X = .00956/(3.78 \times 10^{24} \times .000363) \]
\[ X = 6.97 \times 10^{-24}; \quad \text{pFe} = 23.16 \]

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

H₂O, H⁺, OH⁻, Ca²⁺, NO₃⁻, Mg²⁺, Cl⁻, Na⁺, H₂CO₃, HCO₃⁻, CO₃²⁻

Species precipitating?

CaCO₃, MgCO₃

11 aqueous species, 2 precipitating species

Equations:

\[ 4.46 \times 10^{-7} = [H^+] [\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] \]
\[ 4.69 \times 10^{-11} = [H^+] [\text{CO}_3^{2-}]/[\text{HCO}_3^-] \]
\[ K_w = [H^+] [\text{OH}^-] \]
\[ 4.5 \times 10^{-9} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] \]
\[ 3.5 \times 10^{-8} = [\text{Mg}^{2+}][\text{CO}_3^{2-}] \]

Charge Balance: [H⁺]+[Na⁺]+2[Ca²⁺]+2[Mg²⁺]=[OH⁻]+[NO₃⁻]+[HCO₃⁻]+2[CO₃²⁻]

Mass Balance eqns:

\[ [\text{NO}_3^-] = (1 \text{ M} \times 1 \text{ ml} \times 2)/7 \text{ ml} \]
\[ [\text{Cl}^-] = (.5 \text{ M} \times 2 \text{ ml} \times 2)/7 \text{ ml} \]
\[ [\text{Na}^+] = (.25 \text{ M} \times 3 \text{ ml} \times 2)/7 \text{ ml} \]
\[ [\text{Ca}^{2+}] = (1 \text{ M} \times 1 \text{ ml} \times 1)/7 \text{ ml} \] If and only if no precipitate forms
\[ [\text{Mg}^{2+}] = (.5 \text{ M} \times 2 \text{ ml} \times 1)/7 \text{ ml} \] If and only if no precipitate forms
\[ [\text{H}_2\text{CO}_3]+[\text{HCO}_3^-]+[\text{CO}_3^{2-}] = (.25 \text{ M} \times 3 \text{ ml} \times 1) + (.25 \text{ M} \times 1 \text{ ml x 1}))/7 \text{ ml} \]
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 = 55.5M I said +2 points even for the obvious ones!
\[[\text{NO}_3^-]\] = .286 M
\[[\text{Cl}^-]\] = .286 M
\[[\text{Na}^+]\] = .214 M
\[[\text{Ca}^{2+}]^*\] = .142M
\[[\text{Mg}^{2+}]^*\] = .142M
Total carbonate * = (.75+.25)/7 = .142M

Trial assumptions

\(\text{H}_2\text{CO}_3 + \text{CO}_3^{2-} \rightarrow 2\text{HCO}_3^-\)
The reaction of a weak base and a weak acid. Never did this before, does this make sense?

Weak acid
\(\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-\) \(\text{Ka} = 4.46\times10^{-7}\)

Weak base
\(\text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{OH}^-\) \(\text{Kb} = \text{K}_w/\text{K}_a = 1\times10^{-14}/4.69\times10^{-11} = 2.13\times10^{-4}\)

Net from adding these equations is:
\(\text{H}_2\text{CO}_3 + \text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{H}^+ + \text{OH}^-\)

To get rid of \(\text{H}^+\) and \(\text{OH}^-\) products we need 1 more reaction

Weak acid
\(\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^-\) \(\text{Ka} = 4.46\times10^{-7}\)

Weak base
\(\text{CO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{OH}^-\) \(\text{Kb} = \text{K}_w/\text{K}_a = 1\times10^{-14}/4.69\times10^{-11} = 2.13\times10^{-4}\)
Reverse of \(K_w\)
\(\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}\) \(1/\text{K}_w = 1\times10^{-14}\)

Net now
\(\text{H}_2\text{CO}_3 + \text{CO}_3^{2-} + \text{H}^+ + \text{OH}^- + \text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + \text{H}^+ + \text{OH}^- + \text{H}_2\text{O}\) \(\text{K} = \text{K}_a \times \text{K}_b \times 1/\text{K}_w\)
\(\text{H}_2\text{CO}_3 + \text{CO}_3^{2-} \rightarrow 2\text{HCO}_3^-\) \(\text{K} = (4.46\times10^{-7} \times 2.13\times10^{-4})/1\times10^{-14}\)
\(\text{K} = 9,500\)

Not a great \(K\), but enough to show that reaction will go forward

If above is true

Mole \(\text{H}_2\text{CO}_3\) = .25 mmole
Mole \(\text{CO}_3^{2-}\) = .75 mmole

RXN table
\[ \text{H}_2\text{CO}_3 + \text{CO}_3^{2-} \rightarrow 2\text{HCO}_3^- \]
\[
\begin{array}{ccc}
.25 & .75 \\
-.25 & -.25 & +.5
\end{array}
\]
Net 0 .5 .5

after reaction
pH = pKa2 + 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 Ksp with [Mg] and [Ca]
if ppt forms, then this may be difficult to solve
if ppt doesn’t form we solve for everything.

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

\[ K_{\text{SP MgCO}_3} = 5\times10^{-8} \]

\[ Q > K \text{ Too many products, ppt will form} \]

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

\[ K_{\text{SP CaCO}_3} = 4.5\times10^{-9} \]

\[ Q > K \text{ Too many products, ppt will form} \]

As ppt forms, \text{CO}_3^{2-} is pulled from solution, pH shifts, \text{HCO}_3^- changes to \text{CO}_3^{2-} and everything goes to H— in a handbasket as far as our calculations are concerned.