Exam 1 **Name:**
Chem 311
Fall 2004

Each problem is worth 25 pts. Choose to answer any 4 of the 6 problems!!!!!

1) Calculate the pH of a 0.0500 M solution of Phenylacetic acid.

Phenylacetic acid (HP) is a weak acid.

$HP + H_2O \leftrightarrow P^- + H_3O^+$

$Ka = 4.90*10^{-5} = [P^-][H_3O^+] / [HP] = x^2/(0.0500-x) \approx x^2/(0.0500)$

$X = [H_3O^+] = 0.0015652$ M

pH = 2.805417 = 2.805

$\alpha_{P-} = 0.0015652/0.05 = 0.03$, assumption are justified!!!

2) A 100.00 ml aliquot of a 0.02056 M solution of Threonine is titrated with 0.1025 M NaOH. Calculate the pH at the equivalence point of this titration.

The threonine system consists of T^-, HT, H_2T^+

The intermediate species is the neutral form. A solution of threonine is a solution of T.

Titration reaction:

$$HT + OH^- \rightarrow T^- + H_2O$$

At the equivalence point all of the HT is converted to T^-.

$V^* = (100.00 \text{ ml})(0.02056 \text{ M})/(0.1025 \text{ M}) = 20.0585 \text{ ml}$

$F^{T-} = (100.00 \text{ ml})^* (0.02056 \text{ M}) / (100.00 + 20.0585 \text{ ml}) = 0.01712498 \text{ M}$

Pertinent equilibrium at equivalence point:

$$T^- + H_2O \leftrightarrow HT + OH^-$$

$K_{b1} = K_w/K_{a2} = 1.01*10^{-14}/7.94*10^{-10} = [OH^-][HT]/[T^-]$

$= x^2/(0.01712498-x) \approx x^2/0.01712498$

$x = [OH^-] = 4.667297*10^{-4} \text{ M}$

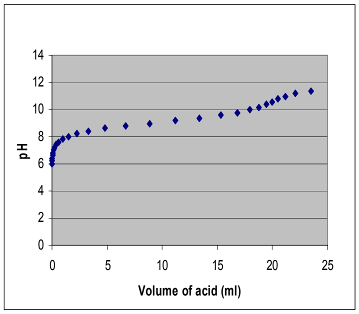
$[H_3O^+] = K_w/[OH^-] = 2.16399*10^{-11} \text{ M}$

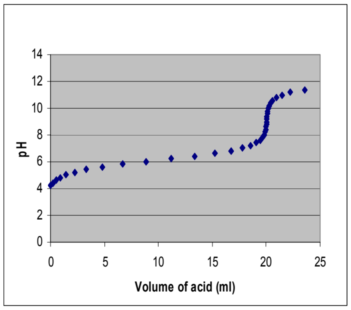
pH = 10.665

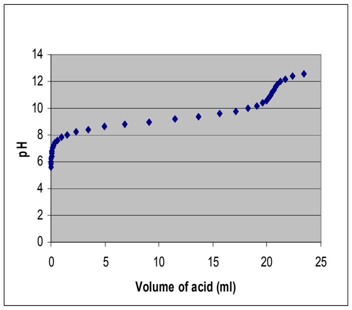
$\alpha_{HT} = 4.667*10^{-4}/.01712 = 0.027$ (assumption valid)

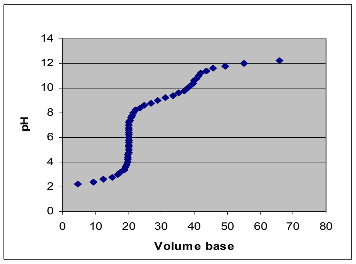
Place a check mark in the titration curve that best represents the Threonine titration above.

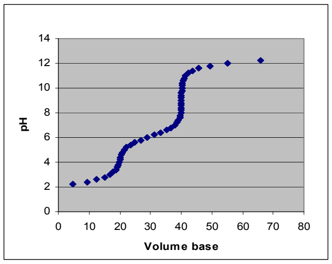
The first one is correct. pH(equiv pt) = 10.7; $pK_{a2} = 9.1$; pH@25 ml = 11.6

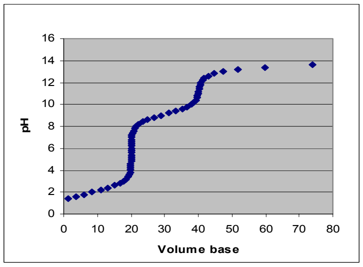












3) A buffer is prepared by dissolving some NaH_2PO_4 in 50.00 ml of a 0.2513 M NaOH and diluting to a total volume of 100 ml. How many grams of NaH_2PO_4 are needed to give a buffer with a pH of 7.40.

Molecular weight (NaH_2PO_4) = 119.9772 g/mol

pH is closest to $pKa_{2,}$ so we must have a mixture of HPO_4^{2-} and $H_2PO_4^-$

$pH = pKa2 + \log (\text{mol } HPO_4^{2-}/\text{mol } H_2PO_4^-)$

initial mol $H_2PO_4^-$ = 50.00 ml * 0.2513 M = 12.565 mmol OH-

	$H_2PO_4^-$	+	OH^-	→	HPO_4^{2-}	+	H_2O
Initial	x		12.565		0		
Final	x-12.565				12.565		

$7.40 = 7.199 + \log [12.565/(x-12.565)]$

x = mmol OH^- added

$1.5885 = 12.565/(x-12.565)$
$1.5885x – 19.9595 = 12.565$
$1.5885x = 32.5245$

x = 20.475 mmol OH^-

grams of NaH_2PO_4 = (20.475 mmol OH^-)(119.9772 g/mol)/1000 = 2.46 g

4) A TRIS {Tris(dyhydroxymethyl)aminomethane}buffer is prepared at a pH of 8.00. Calculate the alpha fraction of the TRIS-H$^+$ species in this solution.

This is a monoprotic system.

Ka =$8.41*10^{-9}$
$[H^+] = 10^{-pH} = 1.0*10^{-8}$ M
$\alpha_{TrisH+} = [H^+] / (ka + [H^+])$ {chapter 11)

$\alpha_{TrisH+} = 0.54$

5) Approximately 0.1 g of Silver chromate, Ag_2CrO_4, is added to 100.00 ml of a 0.01667 M Na_2CrO_4 solution. *Taking into account activities*, calculate the $[Ag^+]$ of the resulting solution after equilibrium has been reached.

Na_2CrO_4 is a soluble salt.

$Ksp(Ag_2CrO_4) = 1.2*10^{-12} = \mathcal{A}_{Ag+}{}^2\mathcal{A}_{CrO42-} = \gamma^2{}_{Ag+}[Ag^+]^2\gamma_{CrO4}[CrO_4{}^{2-}]$

$[Ag^+] = 2x$
$[CrO_4{}^{2-}] = 0.01667 + x$

$\mu = ½\ \{[Na^+](+1)^2 + [CrO_4{}^{2-}](-2)^2 = 0.050$ M

$\gamma_{Ag+@\mu=.050} = 0.80$
$\gamma_{CrO4@\mu=.050} = 0.445$

$1.2*10^{-12} = (0.80)^2\ x^2\ (0.445)(0.01677 + x) \approx (0.80)^2\ x^2\ (0.740)(0.01667)$

$x = 1.6*10^{-5}$ M $<<< 0.01677$; assumption justified

$[Ag^+] = 3.2*10^{-5}$ M

6) A fellow student is designing an experiment that uses a 0.1 M $AgNO_3$ solution to measure $[Cl^-]$ by a precipitation titration. The student wants to standardize the $AgNO_3$ solution using an EDTA titration. However, Figure 13-13 suggests that there is no appropriate indictor for the Ag^+ ion.

As a result the student proposes to perform a displacement titration with standard $Mg(EDTA)^{2-}$.

$$Ag^+ + Mg(EDTA)^{2-} \rightarrow Ag(EDTA)^{3-} + Mg^{2+}$$

Followed by titration of the released Mg^{2+} with standardized EDTA to a Erichrome Black T endpoint.

Why is this proposal flawed?

This displacement reaction is not favorable
A displacement reaction using $Mg(EDTA)^{2-}$ can only work if the $K_f(X) >> K_f(Mg^{2+})$

$\text{Log } K_f(Mg^{2+}) = 8.79$
$\text{Log } K_f(Ag^+) = 7.32$