

Chem 311
Exam 1
October 10, 2003

Name:

Each problem is worth 20 pts. Answer any 5 of the following 7 problems.

- 1) Calculate the pH of a solution prepared by dissolving 1.471 g of Succinic acid with about 50 ml of de-ionized water in a 100.00 ml volumetric flask and subsequently diluting to the 100.00 ml mark with de-ionized water.

$$F_{\text{HA}} = 1.471 \text{ g} \cdot (1 \text{ mol} / (6 \cdot 1.00794 + 4 \cdot 15.9994 + 12 \cdot 4 \text{ g})) \cdot (1 / 0.1 \text{ L}) = 0.124613 \text{ M}$$

$$K_a = [\text{H}^+]^2 / F$$

$$[\text{H}^+] = \sqrt{(0.0000621) \cdot (0.124613)} = 0.002782 \text{ M}$$

assumption are justified

$$\text{pH} = -\log(0.002782) = 2.556$$

- 2) 25.00 ml of a 0.2502 M solution of Histidine-HCl (HHis^+) is titrated with 0.1042 M KOH. Calculate the pH at the first equivalence point.

$$V^* = 25 \cdot 0.2502 / 0.1042 = 60.02879079 \text{ ml}$$

$$F_{\text{His@eq}} = 0.2502 \cdot 25 / (25 + 60.02879079) = 0.073563318 \text{ M}$$

$$[\text{H}^+] = \left(\frac{(K_1 K_2 F + K_w K_1)}{(K_1 + F)} \right)^{1/2} = \left(\frac{(0.00000095 \cdot 0.0000000083 \cdot 68 + 0.00000095 \cdot 0.0000000000000101)}{68} \right)^{0.5} = 2.80826 \text{E-}08 \text{ M}$$

$$\text{pH} = -\log(2.80826 \text{E-}08) = 7.55$$

- 3) 100.00 ml of a 1.26 mM solution of hydroxylamine is titrated with 0.01372 M HCl. Calculate the pH at the equivalence point.

$$V^* = 1.26 \cdot 100 / 13.72 = 9.183673469 \text{ ml}$$

$$F_{\text{HB+@eq pt}} = 1.26 \cdot 100 / (100 + 9.18367) = 1.154018692 \text{ mM}$$

$$[\text{H}^+] = (K_a F)^{1/2} = \sqrt{(0.0000011 \cdot 1.154018692 / 1000)} = 3.56289 \text{E-}05 \text{ M}$$

$$\text{pH} = -\log(3.56289 \text{E-}05) = 4.448$$

- 4) **This problem refers to the titration in the previous problem.**
Calculate the pH after the addition of 3.53 ml of the dilute HCl solution.

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \left\{ \frac{(\text{mol B})}{(\text{mol HB}^+)} \right\} \\ &= 5.96 + \text{LOG} \left\{ \frac{(100 \cdot 1.26 - 3.53 \cdot 13.72)}{(3.53 \cdot 13.72)} \right\} = 6.17 \end{aligned}$$

- 5) Estimate the pH of a 0.0253 mM solution of HNO₃ (strong acid) that contains 0.0500 M of NaCl. **(Must take into account activities)**

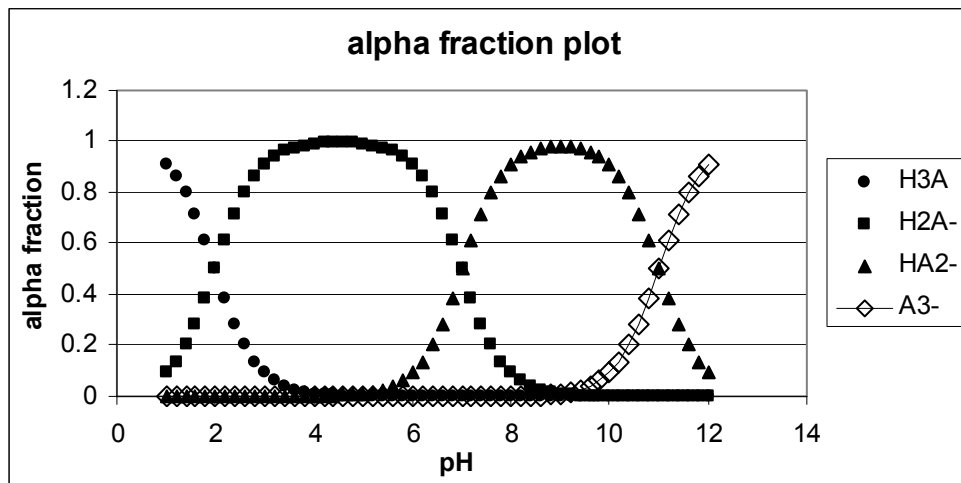
$$\begin{aligned} \mu &= \frac{1}{2}((.05)(1)^2 + (.05)(-1)^2) = 0.05 \text{ M} \\ \gamma_{\text{H}^+ @ m=0.05 \text{ M}} &= 0.83 \\ \text{pH} &= -\log \{ [\text{H}^+] \gamma \} = -\log \{ (2.53 \cdot 10^{-5}) \cdot (0.83) \} = 4.66 \end{aligned}$$

- 6) **There are two parts to this problem.**
Part A: Estimate the Kb's for the polyprotic system.

$$14 = \text{p}K_{a1} + \text{p}K_{b3} = \text{p}K_{a2} + \text{p}K_{b2} = \text{p}K_{a3} + \text{p}K_{b1}$$

$\text{p}K_{a1} = 2$	$\text{p}K_{b3} = 12$
$\text{p}K_{a2} = 7$	$\text{p}K_{b2} = 7$
$\text{p}K_{a3} = 11$	$\text{p}K_{b1} = 3$

$K_{a1} = 10^{-2}$	$K_{b3} = 10^{-12}$
$K_{a2} = 10^{-7}$	$K_{b2} = 10^{-7}$
$K_{a3} = 10^{-11}$	$K_{b1} = 10^{-3}$



Part B: A 0.368 M solution of NaH₂A is titrated with dilute NaOH. **Estimate** (not calculate!!!!) the pH at the start of the titration (ie. 0.00 ml of NaOH added).

At the peak of the H₂A⁻ curve in the alpha plot; About pH = 4.5
Or $\frac{1}{2}(\text{p}K_{a1} + \text{p}K_{a2}) = 4.5$

- 7) In preparing a dilute solution (0.0100 M) of H_3PO_4 a chemist added the appropriate amount of concentrated H_3PO_4 to about 450 ml of de-ionized water in a 500 ml volumetric flask. She then mistakenly diluted to the mark with dilute solution of NaOH. Using a pH meter she measured the pH of the resulting solution (pH = 7.65). Calculate the concentration of $[\text{H}_3\text{PO}_4]$ in this solution. (HINT: use of alpha fraction equation is suggested).

$$\text{pH} = 7.65$$

$$[\text{H}^+] = 10^{-7.65} =$$

$$\alpha_{\text{H}_3\text{PO}_4} = \frac{[\text{H}^+]^3}{\{ [\text{H}^+]^3 + [\text{H}^+]^2\text{Ka}_1 + [\text{H}^+]\text{Ka}_1\text{Ka}_2 + \text{Ka}_1\text{Ka}_2\text{Ka}_3 \}}$$
$$= 8.24\text{E-}07$$

$$[\text{H}_3\text{PO}_4] = F * \alpha_{\text{H}_3\text{PO}_4} = 0.01 * 8.24\text{E-}07 = 8.2\text{E-}09 \text{ M}$$