Name Key

CH 222 Quantitative Analysis Test 2 March 18, 2014

Be sure to show units in your numerical work. You must express answers with the correct number of digits!

1. For a weak acid, write its dissociation reaction and write the hydrolysis reaction of its conjugate base. Given than pH + pOH =14, show that $pK_a + pK_b = 14$.

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \quad K_a$$
$$A^- + H_2O \rightleftharpoons HA + OH^- \quad K_b$$
$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad K_aK_b$$
$$2H_2O \rightleftharpoons H_3O^+ + OH^- \quad K_w, \text{ so } K_w = K_aK_b$$
$$-\log_{10}(K_w = K_aK_b) = -\log_{10} K_w = pK_a + pK_b$$
$$= 14 = pK_a + pK_b$$

2. A solution containing carbonate species has pH = 8.82. Compute the ratio of $[CO_3^{-2}]$ to $[HCO_3^-]$ in the solution. The two pK_as of carbonic acid listed by Harris are 6.351 and 10.329.

$$pH = pK_{a_2} + \log_{10} \frac{[CO_3^{-2}]}{[HCO_3^-]}$$

$$\frac{[CO_3^{-2}]}{[HCO_3^-]} = 10^{pH - pK_{a_2}}$$

$$pH - pK_{a_2} = 8.82 - 10.329 = -1.51$$

$$\frac{[CO_3^{-2}]}{[HCO_3^-]} = 0.031$$

3. In lab you titrated solutions that contained a mixture of sodium bisulfate ($NaHSO_4$) and citric acid. Based on the observed pH curves, which is the stronger acid? Justify your choice.

The shape of the curve early in a titration of a mixture resembles the titration of $NaHSO_4$, therefore it, $NaHSO_4$, is reacting first with NaOH. So it is the stronger acid.

4. The reaction of acetic acid with methyl amine produces acetate ion and the methylammonium ion. Write the balanced reaction showing structures for each species, and indicate the conjugate acid-base pairs. Given that the K_a of acetic acid is 1.75×10^{-5} and the K_a of methylammonium is 2.3×10^{-11}, compute the K of the reaction.

$K_a = 1.75\times10^{-5}$

$K_a' = 2.3\times10^{-11}$

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad K_a$

$CH_3NH_2 + H_2O \rightleftharpoons CH_3\overset{\oplus}{N}H_3 + OH^- \quad K_b = \frac{K_w}{K_a'}$

$CH_3COOH + CH_3NH_2 \rightleftharpoons CH_3COO^- + CH_3\overset{\oplus}{N}H_3 \quad K_aK_b$

acid — base — conj base — conj acid

$$K = K_aK_b = \frac{K_aK_w}{K_a'} = \frac{1.75\times10^{-5}\ 1\times10^{-14}}{2.3\times10^{-11}}$$

$$= \frac{1.75\ (1)}{2.3} \times 10^{-5-14+11}$$

$$= 0.761 \times 10^{-8} = 7.6\times10^{-9}$$

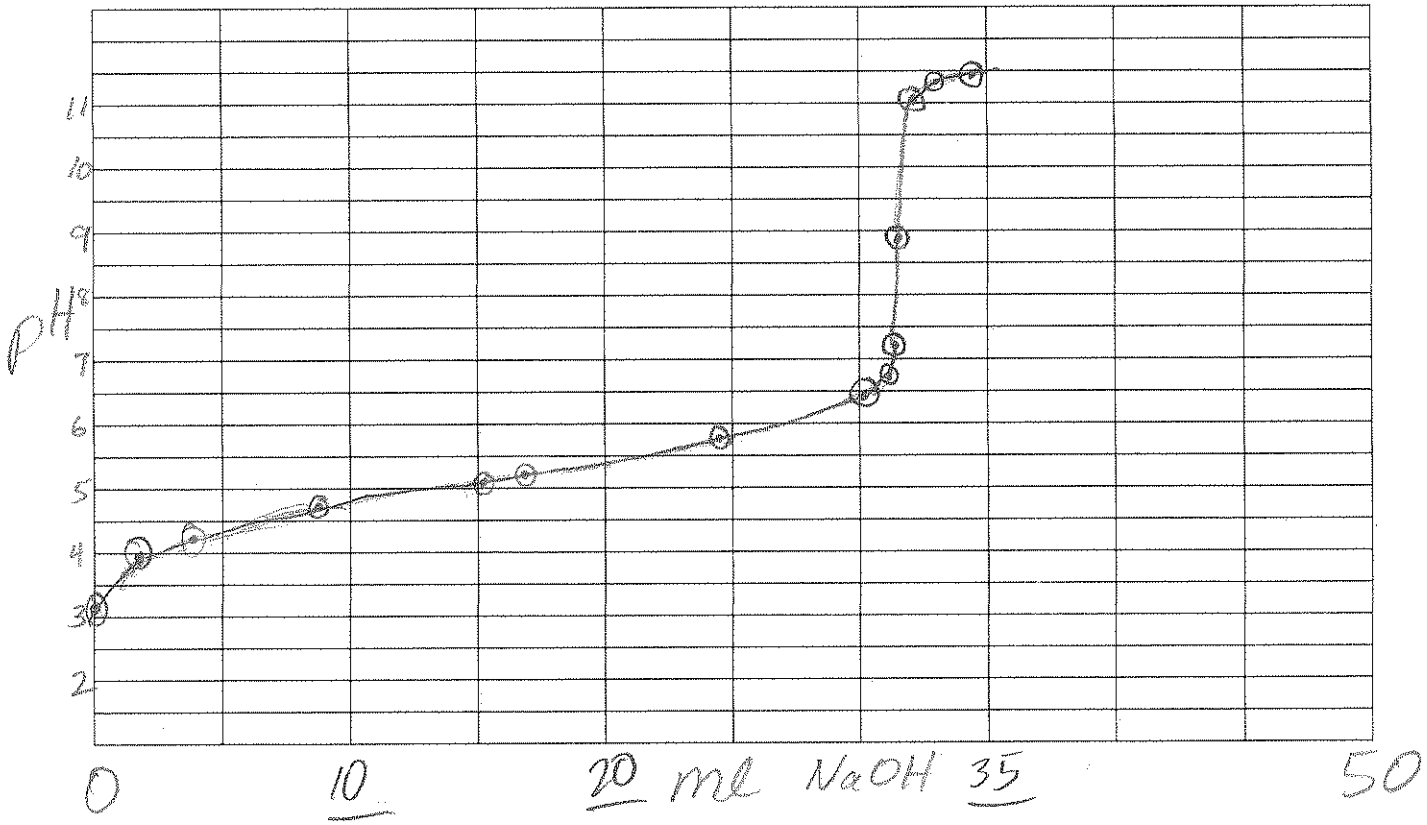
5. On the graph below plot the following titration data to make a curve of pH vs ml titrant. The titration is 25 mls of weak acid vs 0.1000 M NaOH. Examine the curve and compute the molarity of the weak acid and estimate its pKa.

ml	pH
0.00	3.19
0.32	3.41
0.65	3.59
1.62	3.94
3.24	4.25
8.11	4.72
15.56	5.17
16.86	5.23
24.32	5.68
30.80	6.48
31.45	6.71
31.78	6.89
32.10	7.20
32.43	8.89
32.59	11.14
33.07	11.29
33.40	11.37
34.05	11.49

~16.23 ml
$pK_a \sim 5.2$ (pH at half-way point)

sharp break is end point 32.43 ml

$$M_{acid} = \frac{ml_b \, M_b}{ml_a} = \frac{32.43 \; 0.1000}{25.00} = 0.1297 M$$



6. Describe how to prepare a 0.200 M acetate buffer at pH 5.00 using some combination of the following four liquids: pure acetic acid (which is roughly 17 M), deionized water, ~3M HCl, and ~3M NaOH. The pK_a of acetic acid is 4.76. Make any volume you want! But 0.200 M acetate buffer means that the total concentration of all acetate species in the solution should add up to 0.200 M.

$pH = pK_a + \log \frac{[OAc^-]}{[HOAc]}$

$\frac{[OAc^-]}{[HOAc]} = 10^{pH-pK_a} = 10^{0.24} = 1.74$

$[OAc^-] = 1.74\,[HOAc]$

$[OAc^-] + [HOAc] = 0.20\ M$ (20 mmole in 100 ml)

$1.74\,[HOAc] + [HOAc] = 2.74\,[HOAc] = 0.2\ M$

$[HOAc] = \frac{0.2}{2.74} = 0.073\ M$

$[OAc^-] = 0.127\ M$ (12.7 mmole in 100 ml)

For 100 ml buffer
20 mmole HOAc requires
1.18 ml of conc acetic acid

Add 12.7 mmoles NaOH
to create 12.7 mmoles NaOAc
4.23 mls 3M NaOH
dilute to 100 mls w/ $DI\ H_2O$

7. Compute the pH of a solution that you make by dissolving 12 g of Tris and 18 grams of Tris HCl in 237 ml of water. The formula for Tris is $(HOCH_2)_3CNH_2$. The pKa of $TrisH^+$ is 8.075.

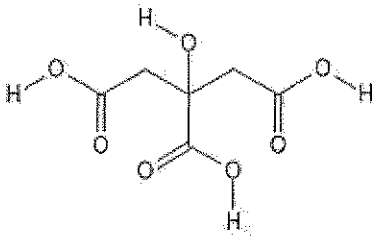
$MW_{Tris} = 121$ $MW_{TrisHCl} = 157$ $V = 237$ ml

$pH = pK_a + \log \frac{[Tris]}{[TrisH^+]} = pK_a + \log \frac{\frac{m_{Tris}}{MW_{Tris} \times V}}{\frac{m_{TrisHCl}}{MW_{TrisHCl} \times V}}$

Vol doesn't matter!

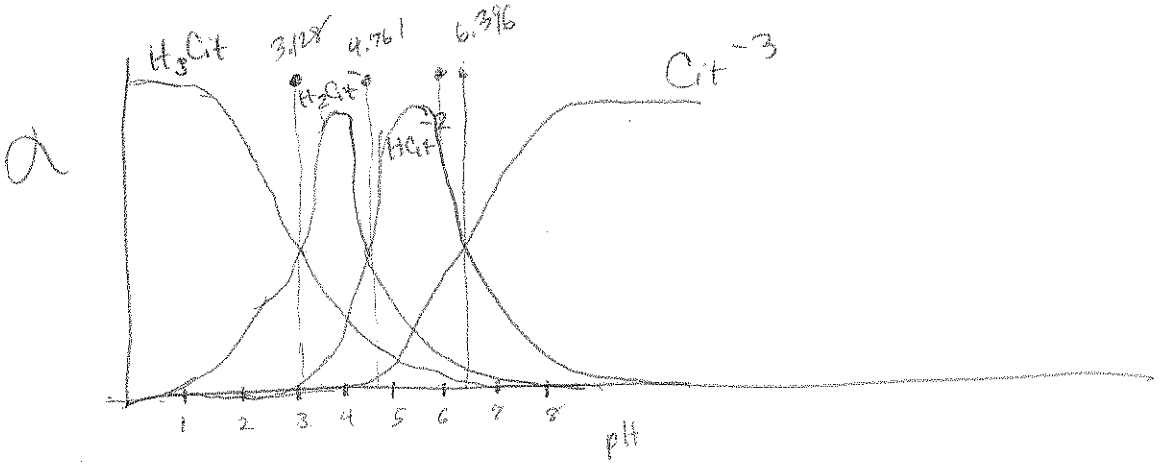
$= 8.075 + \log \frac{12\,g / 121\ g/mol}{18\,g / 157\ g/mol} = 8.075 - 0.063$

$= 8.012$



8. Citric acid is a tricarboxylic acid.
Harris lists its three pKas: 3.128, 4.761, 6.396.

a) Draw a distribution plot that shows the fraction of each species of citrate as a function of pH. Be sure that each curve is clearly labeled.



b) Predict the pH of a solution made by dissolving 3 mmoles of citric acid and 0.8 mmole of trisodium citrate in 120 mls of water. That's H_3Cit and Na_3Cit.

	H_3Cit	H_2Cit^-	$HCit^{-2}$	Cit^{-3}
start	3.0	0	0	0.8
	2.2	0.8	0.8	0
	1.4	2.4	0	0

$H_3Cit + Cit^{-3} \rightarrow H_2Cit^- + HCit^{-2}$

$H_3Cit + HCit^{-2} \rightarrow 2\ H_2Cit^-$

buffer!

$$pH = pKa + \log \frac{[H_2Cit^-]}{[H_3Cit]} = 3.128 + \log \frac{2.4}{1.4} = 3.362$$