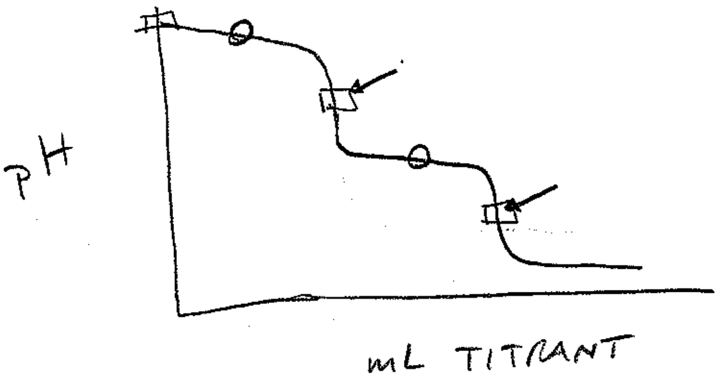
CHEM126-A
Hourly Exam # 2

Spring, '10
Dunnivant

Secret Code KEY

There are 100 points.
Closed book, closed Internet, closed notes, closed cell phone, closed neighbor!
CLARIFICATIONS ARE ALLOWED BUT NO OTHER QUESTIONS!
I'll be in every 30 minutes or so. If you need me come to my lab or office.

1. (10 pts) a) Draw a typical pH (on the y axis) versus mL of titrant added (on the x axis) plot for a diprotic weak base being titrated with a strong acid. b) Place small squares (three are needed) where the buffer capacity is the least. c) Place small circles (two are needed) where the buffer capacity is the greatest. d) Place small arrows (two are needed) at the equivalence points.



2. (5 pts) What two major parameters determine the pH of a weak acid or weak base solution?

- THE pK_a OR pK_b
- THE MOLAR CONC. OF THE ACID OR BASE

3. (10 pts) Starting with

$$HA_{(aq)} + H_2O_{(l)} <===> H_3O^+_{(aq)} + A^-_{(aq)}$$

derive the Henderson-Hasselbalch equation. Show all steps.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]\cancel{[H_2O]}_0}$$

$$K_a = [H_3O^+]\frac{[A^-]}{[HA]}$$

$$[H_3O^+] = K_a\frac{[HA]}{[A^-]}$$

$$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

$$pH = pK_a - \log\frac{[HA]}{[A^-]}$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

4. (10 pts) Two solutions are mixed together, 35.0 mL of a 0.025 M solution of HCl and 15.0 mL of a 0.030 M solution of NaOH. What is the final pH of the mixed solution?

What source of H_3O^+ did you ignore in your calculation?

ACID $(0.0350L)(.025M) = 8.74 \times 10^{-4}$ MOLES H^+

BASE $(0.0150L)(0.030M) = 4.50 \times 10^{-4}$ MOLES OH^-

4.25×10^{-4} H^+ LEFT OVER

$$pH = -\log \left[\frac{4.25 \times 10^{-4}}{.050L}\right] = 2.07$$

5. (5 pts) Acetic acid (CH_3COOH) has a K_a of 1.75×10^{-5}. The chlorinated form of acetic acid, trichloroacetic acid, has a K_a of 0.170. Clearly explain how/why the chlorinated form results in a stronger acid.

THE CHLORINATED FORM HAS MORE ELECTRON
WITH-DRAWING POWER TOWARDS THE 3 Cls.
THIS TAKES THE ELECTRON AWAY FROM
THE COOH GROUP AND ALLOWS THE H
ON THE COOH TO LEAVE..., BEING ACIDIC.

6. (20 pts) Butyric acid, $CH_3CH_2CH_2COOH$, is a weak acid that smells really foul. It has a K_a of 1.51×10^{-5}. 50.0 mL of a 0.0250 M butyric acid solution is titrated with 0.0300 M NaOH. Determine the pH of the solution at the following titration intervals. Conduct your calculations below and on the back but fill in the table with your answers. BE NEAT AND ORDERLY.

mL of Titrant	Resulting pH
0.00	3.21
10.0	4.32
15.0	4.57
mid-point	4.82
30.0	5.23
Equivalence point	8.48
50.0	10.4

$$\overset{HA}{CH_3CH_2CH_2COOH} + H_2O \rightarrow \underset{A^-}{CH_3CH_2CH_2COO^-} + H_3O^+$$

INITIAL pH

	HA	$\rightarrow$ A^-	$+H_3O^+$
I	.025M	0	0
C	$-x$	$+x$	$+x$
E	$0.025M-x$	$+x$	$+x$

IGNORING $-x$ SINCE IT IS LIKELY SMALL (AND I SAID YOU COULD)

$K_a = 1.51 \times 10^{-5} = \frac{x^2}{.025}$ $x = 6.14 \times 10^{-4} = H_3O^+$

$\boxed{pH = 3.21}$

10.0 mL

IGNORING $-x$ & $+x$, USE H-H EQUATION

$pH = pK_a + \log \frac{A^-}{HA}$

A^- ← EQUALS OH^- ADDED; MOLES OR MOLAR

$(.010 L)(.0300 M) = 3.00 \times 10^{-4}$

HA ← INITIAL MOLES − MOLES OH^- ADDED

$(.050L)(.0250M) - (.010L)(.0300M) = 9.50 \times 10^{-4}$

$pH = -\log(1.51 \times 10^{-5}) + \log \frac{3.00 \times 10^{-4}}{9.50 \times 10^{-4}}$

$= +4.82 \quad - 0.50$

$\boxed{= 4.32}$

15.0 mL

$A^- = OH^-\ ADDED = (.0150L)(.0300M) = 4.50\times10^{-4}$

$HA = HA_{INITIAL} - OH^-_{ADDED}$

$= (.050L)(.0250M) - 4.50\times10^{-4} = 8.00\times10^{-4}$

$pH = pKa + \log \frac{4.50\times10^{-4}}{8.00\times10^{-4}} = \boxed{4.57}$

-0.25

AT MID-EQUIV. PT. $pH = pK_A = \boxed{4.82}$

AT 30.0 mL $A^- = OH^-\ ADDED = (.030L)(0.030M) = 9.00\times10^{-4}$

$HA = HA_i - OH^-_{ADDED}$

$= (0.050L)(0.0250M) - 9.00\times10^{-4} = 3.5\times10^{-4}$

$pH = pKa + \log \frac{9.00\times10^{-4}}{3.5\times10^{-4}}$

$= 4.82 + 0.41 = \boxed{5.23}$

AT EQUIV. PT. $M_1V_1 = M_2V_2 \Rightarrow (.050L)(.0250M) = (.0300M)(XL)$

$X_L = 0.040L$

NEW MOLES OF BASE $= \frac{(0.050L)(0.0250M)}{.040L + .050L} = 0.0139M$ BASE

$K_b = \frac{10^{-14}}{1.51\times10^{-8}}$

$= 6.62\times10^{-10}$

	A^-	HA	OH^-
I	.0139	–	–
C	$-x$	$+x$	$+x$
E	$0.0139-x$	x	x

$K_b = 6.62\times10^{-10} = \frac{x^2}{0.0139 - \cancel{x}}$ SMALL

$x = OH^- = 3.03\times10^{-6}$

$pOH = 5.52$

$\boxed{pH = 8.48}$?

50.0 mL

$OH^-\ EXCESS = OH^- - HA_I$

$= (.050L)(.030M) - (.050L)(.0250M)$

$= 2.50\times10^{-4}$ MOLES OH^- /.1L

$pOH = 3.60$ $\boxed{pH = 11.40}$

7. (20 pts) You are conducting a chemical experiment (no biology concerns are necessary) that requires a pH buffer. You need to buffer 1.00 liter of solution at a pH of 4.89. The concentration of conjugate acid in the 1.00 L needs to be 0.250 M. Answer the follow questions.

a) Which of the following buffers is best to use? Circle the best.

	pKa
Hydrotelluric acid, H_2Te, $K_{a1} = 2.3 \times 10^{-3}$	2.64
Butanoic acid, $CH_3CH_2CH_2COOH$, $K_a = 1.5 \times 10^{-5}$	4.82 ← CLOSEST TO 4.89
Carbonic acid, H_2CO_3, $K_{a1} = 4.3 \times 10^{-7}$	6.37
Hydrosulfuric acid, H_2S, $K_{a1} = 8.9 \times 10^{-8}$	7.05

b) What is the concentration of sodium salt of the conjugate base required to make the buffer solution?

$$pH = pKa + \log \frac{A^-}{HA} \leftarrow \text{FROM ABOVE } 0.250\,M$$

$$4.89 = 4.82 + \log \frac{x}{0.250}$$

$$10^{-4.89} = 10^{-4.82} + \frac{x}{0.250}$$

$$\boxed{X = 0.29\ M}$$

20

c) How many grams of the sodium salt of the conjugate base do you need to weigh out? (for the molecular weight take the conjugate base and add one sodium to it)

SODIUM SALT = $CH_3CH_2CH_2COONa$

gmw = 110.1 g/mol

$$\left(0.29\ \frac{\text{Moles}}{L}\right)(1\ L)\left(\frac{110.1\ g}{mol}\right) = \boxed{\begin{array}{c} 32.0\ g \\ \cancel{23.1}\ g \end{array}}$$ 32

8. (20 pts) You have a large volume (10.0 L) of calcium nitrate waste solution that contains trace amounts of cadmium ion (Cd^{2+}). Most calcium nitrate solutions can be disposed of by pouring them down the drain, but the cadmium must be first removed. You decide to remove the cadmium by precipitating it as the carbonate salt (you add sodium carbonate to form $CdCO_3$). K_{sp} for $CdCO_3 = 1.0 \times 10^{-12}$; K_{sp} for $CaCO_3 = 4.96 \times 10^{-9}$.

a) What concentration of dissolved CO_3^{2-} must you obtain in the 10.0 L of waste to lower the Cd^{2+} concentration to the EPA limit of 2.00 parts per billion or 1.79×10^{-11} M?

Note, ignore pH changes in this problem that, in the real world, will affect your calculations.

$$Cd^{2+} + CO_3^{2-} \rightarrow CdCO_3$$

$$K_{sp} = \underset{\text{DESIRED}}{[Cd^{2+}]}[CO_3^{2-}]$$

$$1.00 \times 10^{-12} = [1.79 \times 10^{-11}][x]$$

$$x = CO_3^{2-} = 0.056 M$$

b) If the initial concentration of Cd^{2+} in the waste solution is 0.010 M, what mass of $CdCO_3$ (in grams) did you precipitate?

≈ 0.010M OR ALL OF IT $[Cd^{2+}] = [CdCO_3]$

$$(.010M\ CdCO_3)(10.L)\left(\frac{174g}{\text{mole } CdCO_3}\right) = 17.4g\ CdCO_3$$

Bonus: There is a minor problem with the approach used in the last question (and it is not the pH problem noted above). Clearly identify it and you will receive extra credit.

YOU WILL ALSO PPt SOME OF THE Ca + THIS WILL REQUIRE THAT MORE Na_2CO_3 BE ADDED.