Name: ____________________

Chem 2113 Test 2 June 28, 2002

Questions are worth 25 points each. OMIT ONE QUESTION by clearly writing OMIT in the space provided for your work. If you fail to mark OMIT on a question I will omit the last question of the test. Show your work and circle your answers for full credit.

1. Calculate the pH of the following solutions:

   0.0025 M $HClO_4$

   Since we have a strong acid, we can assume complete dissociation
   ∴ $[H^+] = 0.0025M$; pH = 2.60

   0.0025 M sodium benzoate

   The species affecting the pH is the conjugate base of benzoic acid. K_b is therefore equal to ($1.0 \times 10^{-14} / 6.3 \times 10^{-5}$), and $[OH^-] = \sqrt{K_b C_{A^-}} = \sqrt{\left(\frac{1.0x10^{-14}}{6.3x10^{-5}}\right)(0.0025)}$

   $[OH^-] = 6.3 \times 10^{-7}$; pOH = 6.20, and pH = 7.80

   0.050 M $NaHCO_3$ (sodium bicarbonate)

   Sodium bicarbonate is an acid salt, so $[H^+] = \sqrt{K_1 K_2} = \sqrt{(4.3x10^{-7})(4.8x10^{-11})}$;
   $[H^+] = 4.5 \times 10^{-9}$; ∴ pH = 8.34

   A solution prepared by mixing 27.00 mL of 0.1004 M H_3PO_4 and 40.00 mL 0f 0.06777 M Na_2HPO_4

   Reaction : $H_3PO_4 + HPO_4^{2-} \rightarrow 2\ H_2PO_4^{2-}$

I	2.7108	2.7108	0
Δ	-2.7108	-2.7108	+5.4216
F	0	0	5.4216

   ∴ we have an acid salt in solution, and $[H^+] = \sqrt{K_1 K_2} = \sqrt{(1.1x10^{-2})(7.5x10^{-8})}$
   $[H^+] = 2.9 \times 10^{-5}$, and pH = 4.54

   0.0250 M KI

   Nothing causing ΔpH (Group I cation and conj. base of **strong** acid) ∴ pH = 7.00

2. Consider the titration of 50.0 mL of 0.050*M* salicylic acid with 0.050*M* NaOH. Calculate the pH of the solution at the following points along the titration curve:

a) Before any titrant is added;
The only species in solution is a weak acid; but since K_a * 100 > C_{HA}, we must use the quadratic form: $[H^+] = \frac{-K_a + \sqrt{K_a + 4K_aC_{HA}}}{2}$; $[H^+] = 6.6 \times 10^{-3}$
∴ pH = 2.18

b) After 25.0 mL of titrant is added;
From the reaction: $HA + OH^- \rightarrow A^- + H_2O$

	HA	OH^-	A^-
I	2.5	1.25	0
Δ	-1.25	-1.25	+1.25
F	1.25	0	1.25

∴ we have a weak acid and it's conjugate base in solution, and pH = pK_a + log b/a (Because the conjugate acid/base pair is in the same solution, we can ignore concentrations and use millimolar amounts) pH = 3.00 + log (1.25 / 1.25),
∴ pH = 3.00 (Assuming acid dissociation is negligible, which is borderline for this combination of acid/concentration.)

c) After 40.0 mL of titrant is added;
From the reaction: $HA + OH^- \rightarrow A^- + H_2O$

	HA	OH^-	A^-
I	2.5	2.00	0
Δ	-2.00	-2.00	+2.00
F	0.50	0	2.00

∴ weak acid and it's conjugate base in solution; pH = 3.00 + log (2.00 / 0.50),
∴ pH = 3.60 (Assuming acid dissociation is negligible.)

d) After 50.0 mL of titrant is added;
Equivalence point - only A^- in solution, ∴ $[OH^-] = \sqrt{K_b C_{A^-}} = \sqrt{\left(\frac{1.0x10^{-14}}{1.0x10^{-3}}\right)\left(\frac{2.5}{100}\right)}$

$[OH^-] = 5.0 \times 10^{-7}$; pOH = 6.30
∴ pH = 7.70

e) After 60.0 mL of titrant is added.

Only strong base in solution; $[OH^-]$ = 0.5/110 = 0.0045, ∴ pOH = 2.34
∴ pH = 11.66

3. Consider the titration of 25.0 mL of 0.10 M sodium phthalate [$Na_2C_6H_4(COO)_2$] with 0.10 M HCl. Calculate the pH of the solution at the following points along the titration curve:

a) Before any titrant is added;
Assuming phthalic acid is H_2A, we have A^{2-} in solution, which is the conjugate base of HA^- (K_2), $\therefore$ $K_b = K_w / K_2$, and:

$$[OH^-] = \sqrt{K_b C_{A^-}} = \sqrt{\left(\frac{1.0\times10^{-14}}{3.9\times10^{-6}}\right)(0.10)}$$ $[OH^-] = 1.6 \times 10^{-5}$; pOH = 4.80

$\therefore$ <u>pH = 9.20</u>

b) After 12.5 mL of titrant is added;
The reaction is $A^{2-} + HCl \rightarrow HA^- + Cl^-$

	A^{2-}	HCl	HA^-
I	2.5	1.25	0
Δ	-1.25	-1.25	+1.25
F	1.25	0	1.25

$\therefore$ weak acid (HA^-) and it's conjugate base (A^{2-}) in solution; pH = pK_2 + log (b/a)
pH = 5.40 + log (1.25/1.25); $\therefore$ <u>pH = 5.40</u>

c) After 25.0 mL of titrant is added;
The reaction is $A^{2-} + HCl \rightarrow HA^- + Cl^-$

	A^{2-}	HCl	HA^-
I	2.5	2.5	0
Δ	-2.5	-2.5	+2.5
F	0	0	2.5

HA^- in solution (acid salt), $\therefore$ $[H^+] = \sqrt{K_1 K_2} = \sqrt{(1.2\times10^{-3})(3.9\times10^{-6})}$
$[H^+] = 6.8 \times 10^{-5}$; $\therefore$ <u>pH = 4.16</u>

d) After 37.5 mL of titrant is added;
The **first** reaction is $A^{2-} + HCl \rightarrow HA^- + Cl^-$

	A^{2-}	HCl	HA^-
I	2.5	3.75	0
Δ	-2.5	-2.5	+2.5
F	0	1.25	2.5

This gives us the conditions for the **second** reaction: $HA^- + HCl \rightarrow H_2A + Cl^-$
(note that the initial conditions for the second reaction come from the final conditions for the first reaction)

	HA^-	HCl	H_2A
I	2.5	1.25	0
Δ	-1.25	-1.25	+1.25
F	1.25	0	1.25

$\therefore$ weak acid (H_2A) and it's conjugate base (HA^-) in solution; pH = pK_1 + log (b/a)
pH = 2.92 + log (1.25/1.25); $\therefore$ <u>pH = 2.92</u>
(Assuming acid dissociation is negligible, which is borderline for this combination of acid/concentration)

e) After 50.0 mL of titrant is added.
Second equivalence point - only compound in solution is H_2A. Since $H_2A < 100K_1$, we need to use the quadratic form:

$$[H^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a C_{HA}}}{2}$$ $\therefore$ $[H^+] = 5.8 \times 10^{-3}$; <u>pH = 2.24</u>

4. The active ingredient in disulfiriam, a drug used for the treatment of chronic alcoholism, is tetraethylthiurram disulfide. This drug has a molecular weight of 296.55, and contains four (4) sulfur atoms per molecule. The sulfur in a 0.4329 g sample of disulfiriam preparation was oxidized to SO_2, which was absorbed in H_2O_2 to give H_2SO_4.The acid was treated with 22.13 mL of 0.03736 M NaOH. Calculate the percentage tetraethylthiurram disulfide in the preparation.

Starting with what we know...

22.13 mL * 0.03736 mmol/mL = 0.8268 mmol NaOH

The reaction with sulfuric acid : $H_2SO_4 + 2NaOH \rightarrow 2H_2O + Na_2SO_4$

∴ 0.8268 mmol NaOH / 2 = 0.4134 mmol H_2SO_4 = 0.4134 mmol S

There are 4 atoms of sulfur per molecule of tetraethylthiurram disulfide (TET)

∴ 0.4134 mmol S / 4 = 0.1033 mmol TET

0.1033 mmol TET * 296.55 mg/mmol = 30.65 mg TET

(30.65 mg TET / 432.9 mg sample) x 100% = 7.080% TET

5. A 1.291 sample containing $(NH_4)_2SO_4$, NH_4NO_3, and inert material was diluted to 250.0 mL in a volumetric flask. A 50.00 mL aliquot was then made basic, and the liberated ammonia was distilled into 30.00 mL of 0.08421*M* HCl. After this reaction was complete, the excess HCl was titrated with 10.17 mL of 0.08802*M* NaOH. A 25.00 mL aliquot of the sample was then obtained, made basic, and the NO_3^- was reduced to NH_3 with Devarda's alloy. This aliquot was then distilled into 30.00 mL of the standard acid. It required 14.16 mL of the standard base to react with the excess acid from the second distillation. Calculate the percent $(NH_4)_2SO_4$ and NH_4NO_3 present in the sample.

FOR THE FIRST (50.00 mL) ALIQUOT:

Initially, 30.00 mL x 0.08421 mmol HCl/mL = 2.526 mmol HCl
Excess HCl was titrated with NaOH [Reaction: HCl + NaOH $\rightarrow$ H_2O + NaCl]
10.17 mL x 0.08802 mmol NaOH/mL = 0.8952 mmol NaOH = 0.8952 mmol HCl
HCl reacted: 2.526 - 0.8952 = 1.631 mmol HCl reacted
The reaction with the analyte: HCl + NH_3 $\rightarrow$ NH_4Cl; $\therefore$ 1.631 mmol NH_3 were present.

FOR THE SECOND (25.00 mL) ALIQUOT:

Initially, 30.00 mL x 0.08421 mmol HCl/mL = 2.526 mmol HCl
Excess HCl was titrated with NaOH [Reaction: HCl + NaOH $\rightarrow$ H_2O + NaCl]
14.16 mL x 0.08802 mmol NaOH/mL = 1.246 mmol NaOH = 1.246 mmol HCl
HCl reacted: 2.526 - 1.246 = 1.280 mmol HCl reacted
The reaction with the analyte: HCl + NH_3 $\rightarrow$ NH_4Cl; $\therefore$ 1.280 mmol NH_3 were present.

Because the second aliquot was ½ the size of the first (25/50) we must multiply the mmol NH_3 by 2 for comparison to the first aliquot:

1.280 mmol NH_3 x 2 = 2.560 mmol NH_3 in a 50.00 mL aliquot

'Extra' NH_3 = 2.560 - 1.631 = 0.929 mmol. The source of this 'extra' ammonia was the reduction of nitrate, $\therefore$ there were 0.929 mmol NO_3^- in the 50.00 mL aliquot, $\therefore$ 0.929 mmol NH_4NO_3 in the 50.00 mL aliquot.

0.929 mmol x (250.0 mL/50.00 mL) = 4.64 mmol NH_4NO_3 in the original sample
4.64 mmol NH_4NO_3 x (80.0434 mg/mmol) = 372 mg NH_4NO_3
(372 mg NH_4NO_3 / 1,291 mg sample) x 100% = <u>28.8% NH_4NO_3 in the sample</u>

For the first sample, the 1.631 mmol ammonia was from two sources (NH_4NO_3 and $(NH_4)_2SO_4$). We have determined that 0.929 mmol was from the NH_4NO_3, $\therefore$ ammonia from $(NH_4)_2SO_4$ = (1.631 - 0.929) = 0.702 mmol; however, because there are 2 NH_4^+ ions in ammonium sulfate, 0.702 mmol NH_3 / 2 = 0.351 mmol $(NH_4)_2SO_4$.

$\therefore$ 0.351 mmol $(NH_4)_2SO_4$ x (250.0 mL / 50.00 mL) = 1.76 mmol $(NH_4)_2SO_4$ in sample.
1.76 mmol $(NH_4)_2SO_4$ x 132.1405 mg/mmol = 232 mg $(NH_4)_2SO_4$
232 mg $(NH_4)_2SO_4$ / 1,291 mg sample) x 100% = <u>18.0% $(NH_4)_2SO_4$ in sample</u>