Chemistry 20123, **Exam 1** **Answer Key**

March 4, 2009

Pay attention to Significant Figures in all calculations.

1. (20 points) Each of the following substances was used in one of the experiments that you should have performed thus far in Quant lab. For each substance, state the experiment in which it was used and explain its specific function. Use appropriate chemical reactions in your answers whenever possible. Do not exceed the allotted space!

(a) $Fe(NO_3)_3$

Used as indicator in Volhard titration. At the end-point, Fe^{3+} forms a red-colored complex ion with SCN^-.

$$Fe^{3+} + SCN^- \longrightarrow [FeSCN]^{2+}$$

(b) Urea, $(H_2N)_2CO$

The thermal decomposition of urea,

$$(H_2N)_2C{=}O + H_2O \longrightarrow CO_2 + 2\,NH_4^+ + 2\,OH^-$$

was used in the gravimetric Ca experiment. The slow production of OH^- gradually makes the solution basic, leading to the "homogeneous" precipitation of $CaC_2O_4{\cdot}H_2O$.

(c) potassium thiocyanate

A standard solution of KSCN was used as the titrant in the Volhard experiment. A measured excess of $AgNO_3$ was added to the chloride unknown and then the excess Ag^+ was determined by a "back-titration" with KSCN: $Ag^+_{(aq)} + SCN^-_{(aq)} \longrightarrow AgSCN_{(s)}$

(d) nitrobenzene

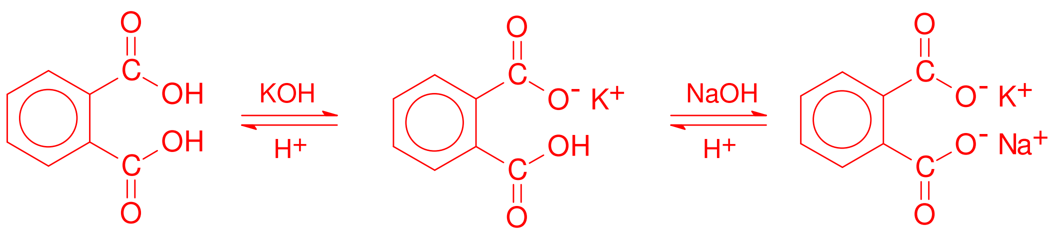
This organic compound was used in the Volhard analysis to coat the AgCl particles, preventing them from re-dissolving and interfering with the AgSCN precipitation titration.

(e) dichlorofluorescein

This is a negatively charged organic compound (anion) that was used as an "adsorption indicator" in the Fajans experiment. It binds (forming a pink-colored complex) to the first excess of Ag^+ ions on the surface of the AgCl precipitate, signaling the end-point.

2. (8 points) What is "KHP"? Draw its chemical structure and explain how it is a good example of a substance that is "amphoteric."

KHP is the mono potassium salt of phthalic acid, a diprotic organic acid. KHP is amphoteric - it reacts with acid to reform the diprotic acid H_2P or with base (e.g., NaOH) to produce the salt of its dianion (e.g., KNaP).



"H_2P" **"KHP"** "KNaP"

3. (8 points) *Briefly* compare and contrast the terms "accuracy" and "precision" as they apply to quantitative analysis.

Accuracy is how close a measured value (or the average of many values) is to the actual (true) value. Influenced by "systematic" errors.

Precision is how close the measured values are to each other. It is a measure of the reproducibility of the measurements. Influenced by "random" errors.

4. (8 points) **SHOW ALL WORK.** In a routine Volhard analysis, a student dissolved a 1.2319-g sample of her unknown in 100 mL of DI water and then added 100.00 mL of 0.1045 M $AgNO_3$. The mixture was then "back titrated" with 0.1096 M KSCN and 28.65 mL was required to reach the end-point. Calculate the mass percentage of NaBr (FM = 102.89) in the unknown.

total moles Ag^+ = (0.1000 L)(0.1045 mole/L) = 0.01045 mole

moles SCN^- = (0.02865 L)(0.1096 mole/L) = 0.003140 mole

moles NaBr = moles Br^- = moles Ag^+ - moles SCN^-

= 0.01045 - 0.003140 = 0.007310 moles

mass NaBr = (0.007310 moles)(102.89 g/mole) = 0.7521 g

percent NaBr = (0.7521 / 1.2319 g) (100 %) = 61.05 %

5. (8 points) **SHOW ALL WORK.** As a TA for Quant lab, you need to prepare 1.00 L of a $Fe_2(SO_4)_3$ (FM = 400.0) solution that has a pFe value of 2.50. Determine the mass of $Fe_2(SO_4)_3$ that you would need and briefly describe how you would prepare the solution.

$[Fe^{3+}] = 10^{-2.50} = 3.16 \times 10^{-3}$ moles/L

mass of $Fe_2(SO_4)_3$ = (1.00 L) (3.16×10^{-3} moles Fe^{3+}/L) x [1 mole $Fe_2(SO_4)_3$ / 2 mole Fe^{3+}] (400 g/mole)

= 0.63 g (2 sig figs based on pFe value with 2 decimal places)

Weigh out 0.63 g $Fe_2(SO_4)_3$, add it to some DI water in a 1.00 L volumetric flask, mix well, and dilute to the mark.

6. (8 points) **SHOW ALL WORK.** In a typical acid-base procedure, a student dissolved 5.2645 g of dry KHP (FM = 204.22) in some DI water and then diluted to the mark in a 500-mL volumetric flask. He then carefully transferred 100.00 mL of this solution to a clean flask and titrated with 26.75 mL of a $Ba(OH)_2$ solution to the phenolphthalein endpoint. Calculate the molarity of the $Ba(OH)_2$ solution.

2:1 stoichiometry: $2\ KHP + Ba(OH)_2 \longrightarrow 2\ H_2O + BaP + K_2P$

Molarity of KHP = (5.2645 g) (1 mole / 204.22 g) / (0.500 L) = 0.05156 M

moles of KHP used in titration = (0.100 L) (0.05156 mole/L) = 0.005156 mole

moles $Ba(OH)_2$ = (0.005156 mole KHP) [1 mole $Ba(OH)_2$ / 2 mole KHP]

= 0.002578 mole

Molarity of $Ba(OH)_2$ = (0.002578 mole) / (0.02675 L) = 0.09637 M

7. Methylamine, CH_3NH_2 (FM = 31.06) is an organic base with $pK_b = 3.36$. In a Gen Chem acid-base experiment, a 25.00 mL portion of 0.1250 M CH_3NH_3Cl was titrated with 0.1000 M KOH.

(a) (5 points) Consider the ***neutralization*** reaction that occurs during the titration and write ***balanced chemical reactions*** for each of the following.

molecular equation:

$$CH_3NH_3Cl + KOH \longrightarrow KCl + H_2O + CH_3NH_2$$

net-ionic equation:

$$CH_3NH_3^+ + OH^- \longrightarrow H_2O + CH_3NH_2$$

(b) (5 points) **SHOW ALL WORK.** Determine the volume (in mL) of KOH solution that is required to reach the equivalence point.

moles OH^- = moles $CH_3NH_3^+$ = (0.02500 L) (0.1250 mole/L)
= 0.003125 mole

volume of KOH = (0.003125 mole) (1,000 mL / 0.1000 mole)
= 31.25 mL

(c) (10 points) **SHOW ALL WORK.** ***Include the appropriate equilibrium reaction.*** Calculate the pH of the CH_3NH_3Cl solution before the titration is started.

Only the weak acid, $CH_3NH_3^+$, is present initially.

I	$CH_3NH_3^+$	$\rightleftharpoons$	CH_3NH_2 +	H^+
C	0.1250 M		0	0
	- x		+ x	+ x
E	0.1045 - x		x	x

$pK_a = 14 - 3.36 = 10.64$

$K_a = 10^{-10.64} = [CH_3NH_2][H^+] / [CH_3NH_3^+]$

$= 2.29 \times 10^{-11} = x^2 / (0.1250 - x)$ (assume x << 0.1250)

$2.29 \times 10^{-11} \sim x^2 / (0.1250)$

$[H^+] = x \sim 1.69 \times 10^{-6}$ (assumption is OK!)

$pH = -\log(1.69 \times 10^{-6}) = 5.77$

7. continued…..

(d) (10 points) **SHOW ALL WORK.** ***Include the appropriate equilibrium reaction.*** Calculate the pH of the solution after 10.00 mL of titrant is added.

The added OH^- neutralizes some $CH_3NH_3^+$, producing some CH_3NH_2 as shown in the neutralization reaction in part (a) above. Thus, the solution is now a mixture of the weak acid ($CH_3NH_3^+$) and its conjugate base (CH_3NH_2), i.e., a buffer solution. The equilibrium reaction is still K_a:

$$CH_3NH_3^+ \rightleftharpoons CH_3NH_2 + H^+$$

moles KOH = moles $CH_3NH_3^+$ neutralized = mole CH_3NH_2 produced

= (0.0100 L)(0.1000 mole/L) = 0.00100 mole

moles $CH_3NH_3^+$ remaining = initial - amount neutralized

= 0.003125 - 0.00100 = 0.002125 moles

$[H^+] = K_a$ (moles acid) / (moles base)

$= (2.29 \times 10^{-11})$ (0.002125) / (0.00100) $= 4.87 \times 10^{-11}$

$pH = -\log(4.87 \times 10^{-11}) = 10.31$

(e) (10 points) **SHOW ALL WORK.** ***Include appropriate equilibrium reaction.*** Calculate the pH of the solution at the equivalence point.

At the equivalence point, all of the acid, $CH_3NH_3^+$, has been neutralized, leaving only the conjugate base, CH_3NH_2, in solution. The equilibrium is now a base dissociation (K_b).

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

$[CH_3NH_2]$ = (moles CH_3NH_2) / total volume (25 + 31.25 = 56.25 mL)

= (0.003125 mole) (0.05625 L) = 0.0556 M

$K_b = 10^{-3.36} = [CH_3NH_3^+][OH^-] / [CH_3NH_2] = x^2 / (0.0556 - x)$

(assume x << 0.0556)

$4.37 \times 10^{-4} \sim x^2 / 0.0556$

$[OH^-] = x \sim 4.92 \times 10^{-3}$ (assumption is marginal!)

$pOH = -\log(4.92 \times 10^{-3}) = 2.31$ pH = 11.69