# CHEM 36
General Chemistry
## EXAM #3

April 17, 2002

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 INSTRUCTIONS: Read through the entire exam before you begin. Answer all of the questions. For questions involving calculations, show **all** of your work -- **HOW** you arrived at a particular answer is **MORE** important than the answer itself! Circle your final answer to numerical questions.

The entire exam is worth a total of 150 points. Attached are a periodic table and a formula sheet jam-packed with useful stuff. Good Luck!

Page	Possible Points	Points Earned
2	25	*25*
3	25	*25*
4	25	*25*
5	25	*25*
6	20	*20*
7	30	*30*
TOTAL:	*150*	*150*
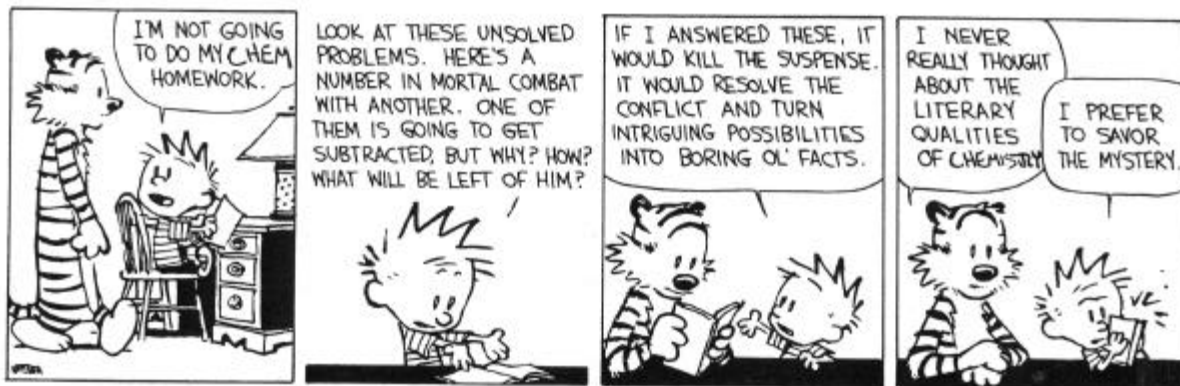
1. a. *[15 pts]* How many grams of aluminum hydroxide will saturate 50.0 mL of water at 25 °C? The solubility-product constant for the dissolution

$$Al(OH)_3 \text{ (s)} \leftrightarrows Al^{3+} \text{ (aq)} + 3OH^- \text{ (aq)}$$
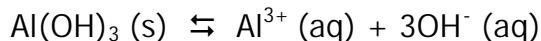
is $K_{sp} = 1.9 \times 10^{-33}$.

From the reaction stoichiometry, we find: $[Al^{3+}] = S$ and $[OH^-] = 3S$
Plugging into the K_{sp} expression: $K_{sp} = [Al^{3+}][OH^-]^3 = 1.9 \times 10^{-33}$
$$S(3S)^3 = 1.9 \times 10^{-33}$$
$$27S^4 = 1.9 \times 10^{-33}$$
$$S = 2.89633 \times 10^{-9} \text{ mol/L}$$

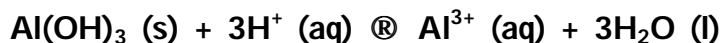**Since S=# mol $Al(OH)_3$ soluble in 1.00 L water, in 50.0 mL:**

0.0500 L x $\underline{\text{2.89633 x } 10^{-9} \text{ mol } Al(OH)_3}$ x $\underline{\text{78.22 g } Al(OH)_3}$ = *1.1327 x 10^{-8} g*
$$ \text{L} \text{mol } Al(OH)_3 Al(OH)_3$$

$$\boxed{\textbf{\textit{1.1 x } 10^{-8} \textbf{\textit{ g } Al(OH)_3}}}$$

b. *[10 pts]* Would $Al(OH)_3$ be (more soluble) or **less soluble** in an *acidic* solution than in pure water? Explain.

$Al(OH)_3$ is a *base* and so will dissolve in acid:

$$Al(OH)_3 \text{ (s)} + 3H^+ \text{ (aq)} ® Al^{3+} \text{ (aq)} + 3H_2O \text{ (l)}$$

So, $Al(OH)_3$ is *more soluble* in acidic solution.

2. The Mohr method is a technique for determining the amount of chloride ion in an unknown sample. It is based on the difference in solubility between silver chloride ($AgCl$; K_{sp} = 1.6 x 10^{-10}) and silver chromate (Ag_2CrO_4; K_{sp} = 1.9 x 10^{-12}). In this method, one adds a small amount of chromate ion to a solution with unknown chloride concentration. By measuring the volume of $AgNO_3$ added before the appearance of the red silver chromate, one can determine the amount of Cl^- originally present.

a. **[10 pts]** Suppose we have a solution that is 0.100 *M* in Cl^- and 0.00250 *M* in CrO_4^{2-}. If we add 0.100 *M* $AgNO_3$ solution drop by drop, will $AgCl$ or Ag_2CrO_4 precipitate first? Justify your answer with a calculation.

We need to calculate [Ag^+] at which each compound will precipitate:

For <u>AgCl</u>:   **[Ag^+] = K_{sp}/[Cl^-] = $\underline{1.6 \times 10^{-10}}$ = *1.6 x 10^{-9} M***
$$\underline{} \text{0.100 }M$$

For <u>Ag_2CrO_4</u>:   **[Ag^+]² = K_{sp}/[CrO_4^{2-}] = $\underline{1.9 \times 10^{-12}}$**
$$\text{2.50 x }10^{-3}\text{ }M$$

[Ag^+] = *2.76 x 10^{-5} M*

Since [Ag^+]$_{AgCl}$ < [Ag^+]$_{Ag2CrO4}$, <u>AgCl will precipitate first</u>

b. **[15 pts]** When Ag_2CrO_4 first appears, what fraction of the Cl^- that was originally present remains?

From *part a*, Ag_2CrO_4 begins to precipitate when [Ag^+] = *2.76 x 10^{-5} M*

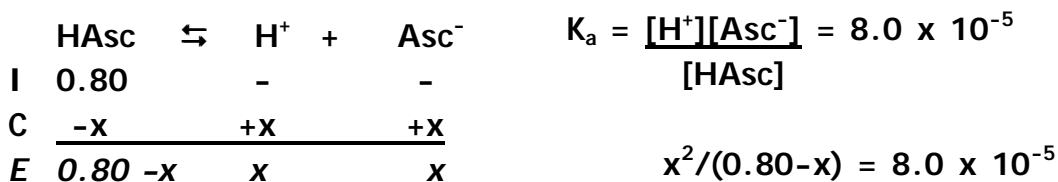**So, [Cl^-] when [Ag^+] = *2.76 x 10^{-5} M*:**

[Cl^-] = K_{sp}/[Ag^+] = $\underline{1.6 \times 10^{-10}}$ = 5.80 x 10^{-6} M
$$\text{2.76 x }10^{-5}$$

Fraction Remaining = $\underline{[Cl^-]_{remaining}}$ = $\underline{5.80 \times 10^{-6}\text{ }M}$ = $\boxed{\textit{5.8 x }10^{-5}}$
$$[Cl^-]_{initial} \qquad \text{0.100 }M$$

3. Vitamin C is ascorbic acid ($HC_6H_7O_6$) which has a $K_a = 8.0 \times 10^{-5}$.

   a. **[10 pts]** Calculate the pH of a 8.0×10^{-1} M solution of ascorbic acid.

	HAsc	$\rightleftharpoons$	H^+	+	Asc^-
I	0.80		-		-
C	-x		+x		+x
E	0.80 -x		x		x

$K_a = \dfrac{[H^+][Asc^-]}{[HAsc]} = 8.0 \times 10^{-5}$

$x^2/(0.80-x) = 8.0 \times 10^{-5}$

Assume: x << 0.80

$x = [H^+] = 8.0 \times 10^{-3}$ *M*

$x^2 = 6.4 \times 10^{-5}$

$x = 8.0 \times 10^{-3}$ *M*

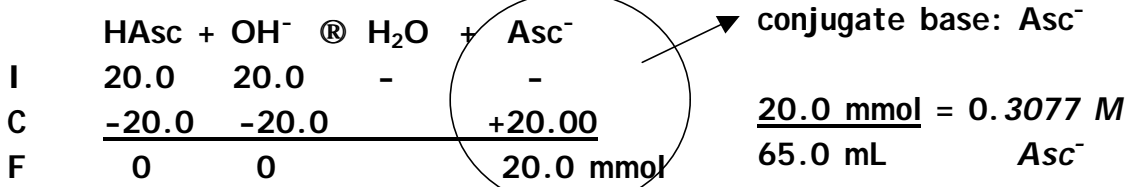pH = $-Log(8.0 \times 10^{-3})$

pH = $\boxed{2.10}$

Assumption checks

   b. **[15 pts]** 40.0 mL of a 0.500 M NaOH solution is added to 25.00 mL of the ascorbic acid solution described above. Calculate the pH of the resultant solution.
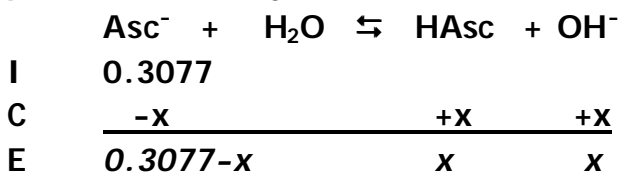
   25.00 mL 0.80 *M* HAsc = *20.0 mmol HAsc*
   40.0 mL 0.500 *M* OH⁻ = *20.0 mmol OH⁻*

   Reaction of a weak acid (HAsc) and a strong base (NaOH) goes to *completion*:

All acid converted to conjugate base: Asc⁻

	HAsc	+	OH⁻	®	H_2O	+	Asc⁻
I	20.0		20.0		-		-
C	-20.0		-20.0				+20.00
F	0		0				20.0 mmol

$\dfrac{20.0 \text{ mmol}}{65.0 \text{ mL}} = 0.3077$ *M* *Asc⁻*

pH determined by Asc⁻ (weak base):

	Asc⁻	+	H_2O	$\rightleftharpoons$	HAsc	+	OH⁻
I	0.3077						
C	-x				+x		+x
E	0.3077-x				x		x

$K_b = \dfrac{[HAsc][OH^-]}{[Asc^-]} = K_w/K_a$

$x^2/(0.3077-x) = 1.25 \times 10^{-10}$

Assume: x << 0.3

$[OH^-] = x = 6.202 \times 10^{-6}$ *M*
pOH = *5.207*
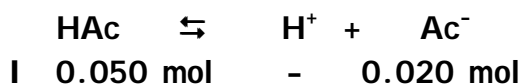pH = 14.00 – pOH = $\boxed{8.79}$

$x^2 = 3.846 \times 10^{-10}$

$x = 6.202 \times 10^{-6}$ (assumption checks)

4. a. **[10 pts]** Calculate the pH in a solution prepared by dissolving 0.050 mol of acetic acid ($K_a = 1.76 \times 10^{-5}$) and 0.020 mol of sodium acetate in water and adjusting the volume to 500. mL.
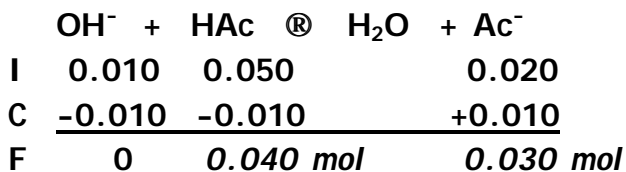
HAc	$\rightleftharpoons$	H^+	+	Ac^-	*This is a buffer!*
I 0.050 mol		–		0.020 mol	*Use Henderson–Hasselbalch:*

pH = pK_a + Log([Ac^-]/[HAc])   *Since vol is constant and x is*
pH = 4.7545 + Log(0.020/0.050)   *much less than 10^{-2} M*
pH = 4.7545 – 0.39794
pH = 4.35655 = $\boxed{4.36}$

b. **[15 pts]** 0.010 mol of NaOH is added to the buffer from part a of this question. Calculate the pH of the solution that results (assume that the total volume of the solution remains at 500. mL).
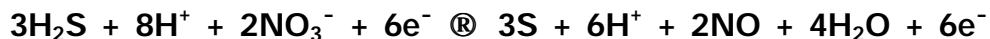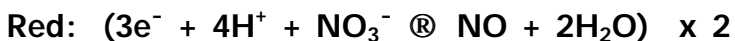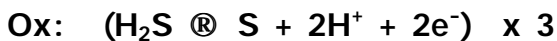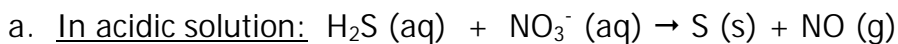
OH^- will react completely with HAc:

	OH^-	+	HAc	$\rightarrow$	H_2O	+	Ac^-	
I	0.010		0.050				0.020	*Still a buffer after reaction, so*
C	-0.010		-0.010				+0.010	*use H–H equation as in part a.*
F	0		0.040 mol				0.030 mol	

pH = pK_a + Log([Ac^-]/[HAc])
pH = 4.7545 + Log(0.030/0.040)
pH = 4.7545 – 0.12494
pH = 4.62955 = $\boxed{4.63}$

5. **[10 pts each]** Complete and balance (using the half-reaction method) the following redox reactions (NOTE: you must show ALL of your work in order to receive credit for your answer!):

   a. <u>In acidic solution:</u> H_2S (aq) + NO_3^- (aq) → S (s) + NO (g)

Ox: $(H_2S → S + 2H^+ + 2e^-)$ x 3
Red: $(3e^- + 4H^+ + NO_3^- → NO + 2H_2O)$ x 2

   $3H_2S + 8H^+ + 2NO_3^- + 6e^- → 3S + 6H^+ + 2NO + 4H_2O + 6e^-$

Finally: $\boxed{3H_2S + 2H^+ + 2NO_3^- → 3S + 2NO + 4H_2O}$

   b. <u>In basic solution:</u> Fe (s) + NiO_2 (s) → $Fe(OH)_2$ (s) + $Ni(OH)_2$ (s)

Ox: $2H_2O + Fe → Fe(OH)_2 + 2H^+ + 2e^-$
Red: $2e^- + 2H^+ + NiO_2 → Ni(OH)_2$

   $2H_2O + Fe + 2e^- + 2H^+ + NiO_2 → Fe(OH)_2 + 2H^+ + 2e^- + Ni(OH)_2$
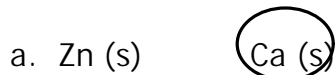
**Finally:** $\boxed{2H_2O + Fe + NiO_2 → Fe(OH)_2 + Ni(OH)_2}$
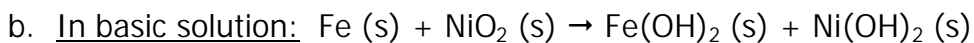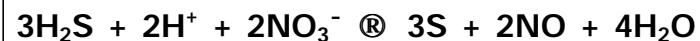
6. **[5 pts]** Using the attached Table of Standard Reduction Potentials, circle the stronger oxidizing agent in each of the following pairs:

   a. Ba^{2+} (aq) $\boxed{Ca^{2+}}$

   b. Cu (s) $\boxed{Fe^{2+}}$
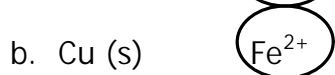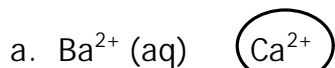
7. **[5 pts]** Using the attached Table of Standard Reduction Potentials, circle the stronger reducing agent in each of the following pairs:
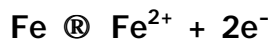
   a. Zn (s) $\boxed{Ca\ (s)}$

   b. $\boxed{I^-\ (aq)}$ F^- (aq)

8. For the following galvanic cell:

$$Fe\ (s)|Fe^{2+}\ (aq)||Ag^+\ (aq)|Ag\ (s)$$
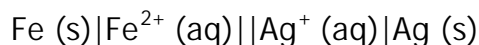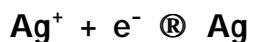
   a. **[5 pts]** Write the balanced chemical equation for the half-reaction occurring at the anode.

   At the anode, *oxidation* occurs:

   $$\boxed{Fe\ ® \ Fe^{2+}\ +\ 2e^-}$$

   b. **[5 pts]** Write the balanced chemical equation for the half-reaction occurring at the cathode.

   At the cathode, *reduction* occurs:

   $$\boxed{Ag^+\ +\ e^-\ ®\ Ag}$$

   c. **[10 pts]** Using the attached Table of Standard Reduction Potentials, calculate the cell voltage, assuming that all reactants and products are in their standard states.

   E^0_{cell} = $E^0_{cathode}$ – E^0_{anode} = E^0_{Ag} – E^0_{Fe} = 0.7996 – (–0.409)

   E^0_{cell} = 1.2086 V = $\boxed{1.209\ V}$

Extra Credit! -- 10 pts

A universal acid/base indicator is easily made by boiling purple cabbage with the resulting aromatic solution producing dramatic color changes over a wide range of pH's. (Gee, this would make a really neat demo!)

Arrange the following five solutions in order of INCREASING pH and give the color of the cabbage indicator solution for each.

        Pure Water
        1.0 M NaOH
        1.0 M HCl
        1.0 M Acetic Acid (HAc)
        1.0 M NH$_3$

Recall that (some of us) DID see this *spectacular* demo ☺:

Low pH ⟶ **High pH**
(acidic)   **(basic)**

   HCl   **®**   *HAc* **®**   *Water*   **®**   *NH$_3$* **®**   *NaOH*
  (RED)   *(PINK)*   *(PURPLE)*   *(GREEN)*   *(YELLOW)*