discard

ANSWER KEY

CHEMISTRY F14O4 PROFESSOR J. MORROW	FIRST EXAM	2/16/00
PRINT NAME, LAST:		
FIRST:		-
I.D.# :		

EACH QUESTION IS WORTH 10 POINTS

1	7	13
2	8	14
3	9	15
4	10	16
5	11	17
6	12	18

COLUMN TOTALS:

EXAM TOTAL (140 pts) _____ OUT OF 100

1) GIVEN THE FOLLOWING STANDARD REDUCTION POTENTIALS (25^oC)

$$Ag(CN)_2^- + e^ Ag^0 + 2 CN^ E^0 = -0.310 V$$
 $Ag^+ + e^ Ag^0$
 $E^0 = -0.800 V$
 $Cu^+ + e^ Cu^0$
 $E^0 = -0.520 V$
 $Cu(CN)_2^- + e^ Cu^0 + 2 CN^ E^0 = -0.440 V$

Calculate ΔG^{0}_{rxn} (in kJ) for the following reaction; SHOW WORK

$$Cu(CN)_{2}^{-} + Ag^{+} \qquad Ag(CN)_{2}^{-} + Cu^{+}$$
a) -14.5 b) 12.5 c) 14.5 d) -12.5 e) 25.0 f) -25.0

$$Cu(CN)_{2}^{-} + e^{-} \qquad Cu^{0} + 2 CN^{-} \qquad E^{0} = -0.440 V$$

$$Ag^{0} + 2 CN^{-} \qquad Ag(CN)_{2}^{-} + e^{-} \qquad E^{0} = +0.310 V$$

$$Ag^{+} + e^{-} \qquad Ag^{0} \qquad E^{0} = -0.800 V$$

$$Cu^{0} \qquad Cu^{+} + e^{-} \qquad E^{0} = -0.520 V$$

$$E^{o}_{cell} = + 0.150 \text{ volts}$$

 $\Delta G^{o}_{rxn} = -nFE^{o} = -(1)(96500)(0.150) = -14475 \text{ J} = -14.5 \text{ kJ}$

GIVE 5 PTS IF ANSWER GIVEN IS \underline{d} ANSWER: $\Delta G_{rxn}^{o} = \underline{a}$

2) For the reaction, $2 \operatorname{Hg}_{(\lambda)} + \operatorname{Cl}_{2(g)} \longrightarrow \operatorname{Hg}_2\operatorname{Cl}_{2(S)}, E^0 = +1.058 \text{ volts.}$ For the reaction, $2 \operatorname{Ag}_{(S)} + \operatorname{Cl}_{2(g)} \longrightarrow 2 \operatorname{AgCl}_{(S)}, E^0 = +1.178 \text{ volts.}$

Calculate the equilibrium constant for the following reaction;

$$2 \operatorname{AgCl}_{(S)} + 2 \operatorname{Hg}_{(\lambda)} \longrightarrow \operatorname{Hg}_2 \operatorname{Cl}_{2(S)} + 2 \operatorname{Ag}_{(S)}$$
$$E^{o}_{cell} = -0.120 \text{ volts} \qquad K = 10^{nE/0.0592} = 10^{(2)(-0.120)/(0.0592)}$$
$$K = 8.83 \times 10^{-5}$$

ANSWER: $K = 8.83 \times 10^{-5}$

3) For the equilibrium reaction, $Ag^+ + 2 CN^- - Ag(CN)_2^-$, the cell notation when the reactants and products are in standard state is;

$$Ag_{(S)} | Ag(CN)_2 (1.00 \text{ M}), CN (1.00 \text{ M}) || Ag^+ (1.00 \text{ M}) || Ag_{(S)} (1.00 \text{ M}$$

If the cell with the new indicated concentrations is now set up,

$$Ag_{(S)}|Ag(CN)_{2}(2.00 \text{ M}), CN(2.00 \text{ M})||Ag^{+}(0.50 \text{ M})|Ag_{(S)}|$$

then,

- a) The reaction will shift to the right
- b) The reaction will shift to the left
- c) The cell voltage will become more positive
- d) The cell voltage will become less positive
- e) The cell voltage will be unchanged
- f) The equilibrium constant will increase in value
- g) The equilibrium constant will decrease in value

YOUR ANSWER(S) IS/ARE: e

4) Given the reaction, $2 \operatorname{Hg}_{(\lambda)} + \operatorname{Cl}_{2(g)} \longrightarrow \operatorname{Hg}_2 \operatorname{Cl}_{2(S)}$

Assume that the standard E^{0} cell voltage is related to the celcius temperature by the following equation and all substances are at standard state. In doing this, you can assume any temperature(s) you desire.

At 298 K (25°C),
$$E^{o}_{cell} = +1.058$$
 volts. SHOW WORK
 $E^{o}_{cell} = 1.058 - 0.00017 (t - 25^{\circ}C)$

The ΔH^{0} (in kJ) for the reaction (as written) at 298 K is; a) -321 b) +107 c) +214 d) -214 e) -107 f) +321

$$\Delta H^{o} = -nF \left\{ E^{o} - T\left(\frac{E^{o}_{2} - E^{o}_{1}}{\Delta T}\right) \right\} = -(2)(96500) \left\{ 1.058 - (298)(-0.00017) \right\} \qquad \Delta H^{o} = -214 \text{ kJ}$$

GIVE 5 PTS IF ANSWER GIVEN IS \underline{e} ANSWER IS: \underline{d}

5) What is the highest pH at which 0.050 M Mn^{2+} remains entirely in a solution that is saturated with H₂S, at a concentration of, [H₂S] = 0.10 M.

Given: For the reaction,
$$MnS_{(S)} = Mn^{2+} + S^{2-}$$
, $K_{sp} = 3.6 \times 10^{-15}$ OR
for the reaction, $MnS_{(S)} + H_2O = Mn^{2+} + HS^{-} + OH^{-}$, $K = 3.0 \times 10^{-14}$
For H_2S : $K_{a1} = 9.2 \times 10^{-8}$ and $K_{a2} = 1.2 \times 10^{-15}$ SHOW WORK
a) 2.9 b) 3.9 c) 4.4 d) 4.9 e) 5.4
 $K = 3.0 \times 10^{-14} = [Mn^{2+}][HS^{-}][OH^{-}] = [Mn^{2+}] \left(\frac{[H_2S]K_{a1}}{[H^{+}]}\right) \left(\frac{K_w}{[H^{+}]}\right)$
 $[H^{+}]^2 = \frac{[Mn^{2+}][H_2S]K_{a1}K_w}{3.0 \times 10^{-14}} = 1.53 \times 10^{-10}$ AND $[H^{+}] = 1.23 \times 10^{-5}$
 $pH = 4.9$

ANSWER IS: <u>d</u>

6) Find among the pH values on the right, the value which most closely

matches the pH of the solutions described in the first column. SHOW ALL WORK FOR <u>PART B</u> ON THIS PAGE!

HINT: In PART B the following reaction occurs, $H_2CO_3 + CO_3^- \longrightarrow 2 HCO_3^-$

	<u>SOLUTION</u>		<u>pH</u>		
A.	0.460 M CH ₃ COOH (HOAc)		5.04		
	that is also 0.0460 M in HNO ₃		4.44		
	-		1.34		
В.	$0.020 \text{ M H}_2\text{CO}_3$ that is also		11.12		0.250
M in Na ₂ CO) ₃	10.72			
	-	5.13			
			2.70		
				7.41	
			2.00		
	(4 pts) Solution A $pH = 1.34$				
		(6 pts) Solution	B pH = 11.1	12	
K_a values: $H_2CO_3 (K_{a1} = 4.3 \times 10^{-7})$, $HCO_3^- (K_{a2} = 4.4 \times 10^{-11})$, $HOAc (K_a = 1.8 \times 10^{-5})$					
Solution A:					

FROM STRONG ACID ONLY: $[H^+] = 0.046 \text{ M}$ pH = 1.34

Solution B:

$$H_{2}CO_{3} + Na_{2}CO_{3} \longrightarrow 2NaHCO_{3}$$
START: 0.020 0.250 0
END: 0 0.230 0.040

$$HCO_{3} \longrightarrow H^{+} + CO_{3}^{2-}$$

$$K_{a2} = 4.4x10^{-11} = \frac{[H^{+}][CO_{3}^{2-}]}{[HCO_{3}^{-}]} = \frac{[H^{+}][0.230]}{[0.040]}$$

$$[H^{+}] = \frac{(4.4x10^{-11})(0.040)}{0.230} = 0.765x10^{-12}$$

$$pH = 11.12$$

7) If 0.77 g of $Cu(IO_3)_2$ will dissolve in 1.0 L of 0.10 M $CuSO_4$ solution, what is the solubility product, K_{sp} , of $Cu(IO_3)_2$? Molar mass = 413.3 g/mol SHOW WORK

a)
$$1.4x10^{-5}$$
 b) $1.4x10^{-6}$ c) $2.6x10^{-7}$ d) $3.5x10^{-7}$ e) $2.6x10^{-8}$
 $K_{sp} = [Cu^{2+}][IO_3^{-}]^2 = (0.10)(\frac{(2)(0.77)}{413.3})^2$
 $K_{sp} = 1.4x10^{-6}$

IF ANSWER GIVEN IS \underline{d} GIVE 5 PTS. ANSWER IS: \underline{b}

THE FOLLOWING INFORMATION IS FOR PROBLEMS 8, 9, AND 10.

40.00 mL of O.100 M methylamine, CH_3NH_2 , is titrated with O.150 M HCl. Calculate the pH; (K_b = 4.0x10⁻⁵ for $CH_3NH_2 + H_2O$ $CH_3NH_3^+ + OH^-$)

8) before any HCl is added.

$$K_{b} = 4.0x10^{-5} = \frac{[CH_{3}NH_{3}^{+}][OH^{-}]}{[CH_{3}NH_{2}]} = \frac{x^{2}}{0.10}$$
$$x = [OH^{-}] = 2.0x10^{-3} \qquad pOH = 2.7 \text{ AND } pH = 11.3$$

pH = 11.3

9) halfway to the equivalence point.

$$pH = pK = -\log(4.0x10^{-5})$$

$$pH = 4.4$$

$$pH = 4.4$$

10) at the equivalence point. (This is now an hydrolysis problem) SHOW WORK AT EQUIVALENCE POINT, VOLUME OF ADDED HCl is 26.7 mL TOTAL VOLUME IS 40.0 + 26.7 = 66.7 mL AND $[CH_3NH_3^+] = \frac{0.0040 \text{ mol}}{0.0667 \text{ L}} = 0.0600 \text{ M}$ $CH_3NH_3^+ + H_2O \longrightarrow CH_3NH_2 + H^+, K_a = \frac{K_w}{K_b} = 2.5 \times 10^{-10} = \frac{[CH_3NH_2][H^+]}{[CH_3NH_3^+]}$ $2.5 \times 10^{-10} = \frac{\chi^2}{0.0600} \qquad x = [H^+] = 3.87 \times 10^{-6} \text{ AND pH} = 5.41$

GIVE 5 PTS FOR pH = 5.30 pH = 5.4111) How many milliliters (mL) of a 0.0500 M NaOH (a strong base) solution should be added to 1.00 L of 0.100 M H₃PO₄ solution, to produce

a buffer of pH = 2.00 ? For H₃PO₄, K_{a1} = 6.67x10⁻³ (SHOW WORK)
GIVEN: H₃PO₄ + OH⁻ (from NaOH)
$$\longrightarrow$$
 H₂PO₄⁻ + H₂O
a) 100 b) 200 c) 400 d) 600 e) 800 f) 900
H₃PO₄ \longrightarrow H⁺ + H₂PO₄⁻ where [H⁺] = 0.010 M
0.10 - x x
K_{a1} = 6.67x10⁻³ = $\frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{(0.0100)[H_2PO_4^-]}{[H_3PO_4]}$
 $\frac{[H_2PO_4^-]}{[H_3PO_4]} = 0.667 = \frac{x}{0.100 - x} \therefore x = 0.0400$
M_{NaOH}V_{NaOH} = 0.0400 \therefore V_{NaOH} = 0.800 L
ANSWER IS: e

12) Given the following cell; $Zn_{(S)}|Zn^{2+}(1 \text{ M})|| H^{+}(? \text{ M})|H_{2(g)}(1 \text{ atm})$. The measured cell voltage is $E_{cell} = 0.653 \text{ V}$. Calculate the pH of the solution in the cathode compartment. HINT: First calculate E_{cell}^{o} . MOLARITIES AND PRESSURE ARE GIVEN IN THE CELL NOTATION ABOVE.

Given:
$$Zn^{2+} + 2e^{-}$$
 $Zn_{(s)}$ $E^{0} = -0.771 V$
a) 1.0 b) 1.5 c) 2.0 d) 3.0 e) 3.5 f) 4.0
REACTION IS: $Zn + 2H^{+}$ $Zn^{2+} + H_{2}$
 $E = E^{0} - \frac{0.0592}{2} \log \frac{[Zn^{2+}]}{[H^{+}]^{2}}$ 0.653 = 0.771 - $\frac{0.0592}{2} \log \frac{1}{[H^{+}]^{2}}$
 $[H^{+}] = 10^{-2} M$ AND $pH = 2.0$ ANSWER IS: c

13) Complete the following table. (For Ca₃(PO₄)₂, K_{sp} = 1.3x1O⁻³²) [Ca²⁺] [PO₄³⁻] <u>1.09x10⁻⁸</u> 1.0x1O⁻⁴ M

15)

6.Ox1O ⁻³ M	<u>2.45x10⁻¹³</u>

14) You have a solution of sodium hydrogen sulfate, NaHSO₄. It's initial concentration is C_0 . The pH = 2.0 for this solution at equilibrium. Calculate the starting concentration, C_0 .

(For the reaction,
$$HSO_4^ H^+ + SO_4^{2-}$$
, $K_{a2} = 0.020$)
 $0.020 = \frac{[H^+][SO_4^{2^-}]}{[HSO_4^-]} = \frac{(0.01)^2}{C_0^{-0.01}}$ $C_0 = 0.015 \text{ M}$
For Ag_2CO_3 , $K_{sp} = 6.2x10^{-12}$. For $AgCl$, $K_{sp} = 2.8x10^{-10}$.

Solid Ag_2CO_3 and solid AgCl are added to a beaker containing 1.00 M Na₂CO_{3(aq)}. Under these conditions the $[CO_3^{2^-}] = 1.00$ M. Calculate the [Cl⁻] in solution when equilibrium is established. ASSUME THE CO₃²⁻ ION DOES NOT HYDROLYZE. SHOW WORK

a)
$$1.1 \times 10^{-4}$$
 b) 1.26×10^{-8} c) 6.7 d) 0.15 e) 2.8×10^{-6}
Ag₂CO₃ \longrightarrow 2 Ag⁺ + CO₃²⁻ \therefore K_{sp} = [Ag⁺]²[CO₃²⁻]
[Ag⁺]² = $\frac{6.2 \times 10^{-12}}{[CO_3^{2^-}]} = \frac{6.2 \times 10^{-12}}{1.0} = 6.2 \times 10^{-12}$ \therefore [Ag⁺] = 2.49 \times 10^{-6}
For AgCl, K_{sp} = $2.8 \times 10^{-10} = [Ag^+][Cl^-] = (2.49 \times 10^{-6})[Cl^-]$
 \therefore [Cl⁻] = $\frac{2.8 \times 10^{-10}}{2.49 \times 10^{-6}} = 1.1 \times 10^{-4}$ M
ANSWER IS: a

16) Given the following K_{sp} values: for $M(OH)_4$, $K_{sp(M)} = 4.Ox10^{-19}$; for $Z(OH)_2$, $K_{sp(Z)} = 1.Ox10^{-14}$. One mole of each of the above solids is placed in a beaker containing 1 (one) liter of pure water. These solids go into equilibrium with their ions. Calculate the pH required for the metal ion concentrations to be equal, $[M^{2+}] = [Z^{3+}]$. (SHOW WORK)

$$K_{sp(M)} = 4.Ox1O^{-19} = [M^{4+}][OH^{-14}] \qquad K_{sp(Z)} = 1.Ox1O^{-14} = [Z^{2+}][OH^{-14}]^{2}$$
$$\frac{K_{sp(M)}}{K_{sp(Z)}} = \frac{4.Ox1O^{-19}}{1.Ox1O^{-14}} = 4.0x10^{-5} = [OH^{-14}]^{2}$$
$$[OH^{-14}] = (4.0x10^{-5})^{1/2} = 6.32x10^{-3} \therefore \text{ pOH} = 2.20 \text{ AND pH} = 11.80$$

 $pH = \underline{e}$

17) Given the following K_a and K_b values: HF (K_a = 10⁻⁴), HCN (K_a = 10⁻⁹), NH₃ (K_b = 10⁻⁵), HOAc (K_a = 10⁻⁵), and HCl (K_a = ∞)

List the following aqueous salts in order of increasing acidity (decreasing basicity); NaF, NH₄Cl, NaCN, NaCl, and NaOAc. THIS IS AN HYDROLYSIS PROBLEM.

LEAST ACIDIC NaCN < NaOAc < NaF < NaCl < NH_4Cl MOST ACIDIC

18) Which graph correctly illustrates the dependence of the cell voltage, E_{cell} , on the pH for the reaction, $2 Ag^+_{(aq)} + H_{2(g)} \longrightarrow 2 Ag_{(s)} + 2 H^+_{(aq)}$. Assume the silver ion remains constant at, $[Ag^+] = 1.0 M$ and the H₂ pressure remains constant at 1 atm.



рΗ