Chem 121 **Name**________________________________
Exam 3 **April 3, 2009**
100 Points

Please follow the instructions for each section of the exam. Show your work on all mathematical problems. Provide answers with the correct units and significant figures. Be concise in your answers to discussion questions.

Complete all of problems 1-4.

1. Of the following, the amphiprotic ion is: (4 points)

   a. HCO_3^-
   b. NH_4^+
   c. CO_3^{2-}
   d. ClO_4^-

   Answer __**a**___

2. The effect of adding 0.001 mol KOH to 1.00 L of a solution that is 0.10M NH_3 and 0.10M NH_4^+ is to: (4 points)

   a. Raise the pH by several units
   b. Raise the pH very slightly
   c. Lower the pH very slightly
   d. Lower the pH by several units

   Answer __**b**___

3. The reaction $2CO_2\ (g) \rightleftarrows 2CO\ (g) + O_2\ (g)$ has $K_c = 2.0 \times 10^{-6}$. Based on this, the reaction must be (4 points)

   a. Product-favored and fast
   b. Reactant-favored and fast
   c. Reactant-favored and slow
   d. None of the above.

   Answer __**d**___

4. A buffer solution is prepared by dissolving 0.200 moles of picolinic acid (a monoprotic acid with $K_a = 4.10 \times 10^{-6}$) and 0.200 moles of sodium picolinate (its conjugate base) in 1.00 L of solution. (15 points).
   a. What is the pH of this buffer?
   b. What will be the new pH after 5 mL of 2.087 M NaOH is added to 100.0 mL of this buffer solution?

   a. To calculate the pH of a buffer solution, we can use the Hendersen-Hasslebach equation (or set up an ICE table).

$$pH = pK_a + \log \frac{[A^-]}{[HA]} = 5.39 + \log \frac{0.200\ M}{0.200\ M} = \mathbf{5.39}$$

   b. mol HA = 100 mL x 0.200M = 20.0 mmol = mol A-
   mol OH^- = 5 mL x 2.087M = 10.44 mmol

	OH^-	+	HT	→	T^-	+	H_2O
Start	10.44 mmol		20.00mmol		20.00		0
End	0		9.56 mmol		30.44 mmol		10.44 mmol

We now have a new solution of A^- and HA and can determine its pH. We could set up an ICE table or use Henderson Hasslebach equation, either way we get the same result:

$$pH = pK_a + \log \frac{[A^-]}{[HA]} = 5.39 + \log \frac{30.44\ mmol}{9.56\ mmol} = \mathbf{5.89}$$

Answer three (3) of problems 5-8. Clearly mark the problem you do not want graded. 15 points each.

5. A solution contains 25.00 mL of 0.0500M NaOH, 15.00 mL of 0.100M HCl, 10.00 mL of 0.100M KOH, 5.00 mL of 0.200M HNO_3, and 10.0 mL of 0.100M NaCl. What is the pH of the solution?

   With the exception of NaCl, which will not contribute to pH, all of these are strong acids and bases. Therefore, the pH will be determined by the amount of H^+ remaining after neutralization:

   mmol OH^- present: (25.00 mL x 0.0500M) + (10.00 mL x 0.100M) = 2.25 mmol OH^- present
   mmol H^+ present: (15.00 mL x 0.100M) + (5.00 mL x 0.200M) = 2.50 mmol H^+ present

   So, 2.50 – 2.25 = 0.25 mmol of H^+ will be present in the 65.00 mL of solution, giving an H^+ concentration of (0.25 mmol)/(65 mL) = 3.85 x 10^{-3} M or a **pH = 2.41**

6. Explain whether the following statement is true or false: “The exothermic reaction below will be spontaneous at all temperatures.”

   $$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$$

   For a reaction to be spontaneous, the free energy change (ΔG) for the reaction must be negative. The ΔG, however, depends on enthalpy and entropy of the reaction by the equation below:

   So, for ΔG to be negative at all temperatures ΔH for the reaction must be negative and ΔS for the reaction must be positive. From the statement, we are told that the reaction is exothermic, corresponding to a negative ΔH. Looking at the reaction, we see that three moles of gaseous reactants are being converted to two moles of gaseous products. This corresponds to s decrease in entropy, or a negative ΔS. Since this does not fit the criteria for spontaneity at all temperatures, the statement is false.

7. Will the precipitation of MgF_2 occur if a 22.5 mg sample of $MgCl_2 \bullet 6H_2O$ (molar mass = 203.29 g/mol) is added to 325 mL of 0.0035M KF? K_{sp} for $MgF_2 = 3.7 \times 10^{-8}$

   Precipitation will occur if $Q > K_{sp}$ for the equilibrium. The equilibrium in question is that for the dissolution of MgF_2:

   $$MgF_2(s) \rightleftarrows Mg^{2+} + 2F^- \qquad K_{sp} = [Mg^{2+}][F^-]^2$$

   So, we need to determine the $[Mg^{2+}]$ and $[F^-]$ in the solution to see if K_{sp} is exceeded.

   $$22.5\text{ mg } MgCl_2 \bullet 6H_2O \times \frac{1\text{ mol } MgCl_2}{203.29\text{g } MgCl_2} \times \frac{1\text{ mol } Mg^{2+}}{1\text{ mol } MgCl_2} = \frac{1.107 \times 10^{-4}\text{ mol } Mg^{2+}}{0.325\text{ L}} = 3.40_6 \times 10^{-4}\text{ M}$$

   Then $Q = [Mg^{2+}][F^-]^2 = (3.40_6 \times 10^{-4}\text{ M})(0.0035\text{M})^2 = 4.17 \times 10^{-9}$

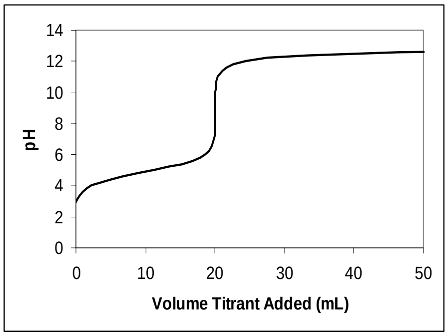
   Since 4.17×10^{-9} is less than 3.7×10^{-8}, no precipitate will form ($Q<K_{sp}$).

8. The curve below corresponds to one of the three titrations listed. Which titration is represented by the titration curve? Explain how you chose the correct answer and ruled out the other two.

   a. The titration of 20 mL of 0.100 M ammonia ($pK_b = 4.75$) with 0.100 M HCl.

   b. The titration of 20 mL of 0.100 M propionic acid ($pK_a = 4.89$) with 0.100 M NaOH

   c. The titration of 20 mL of 0.100 M oxalic acid ($pK_{a1} = 1.27$, $pK_{a2} = 4.28$) with 0.100 M NaOH.



   From the titration curve, the titration starts out acidic, has an equivalence point pH of ~pH 9 at 20 mL and reaches a maximum pH of ~12.5 or so. Which titration conditions does this match. Let's consider each possibility.

   - Since choice (a) is a titration of a weak base with a strong acid, we'd expect the pH to start out basic and get more acidic, which it does not, ruling our (a).
   - Choice (b) is the titration of a weak acid with a strong base, which should start our acidic and have a slightly basic pH at the equivalence point, matching the given data. Plus, we'd expect the pH at 10 mL to be equal to the pK_a (4.89), which appears to be the case.
   - Choice (c) should present two equivalence points, one at 20 mL and a second at 40 mL, since these are not evident in the data, we can rule out (c).

   Therefore, it appears that the data corresponds to the titration described in (b).

In the space below, answer either problem 9 or problem 10. 15 points.

9. An aqueous solution that is 2.00M in $AgNO_3$ is slowly added from a buret to an aqueous solution of 0.0100M Cl^- and 0.250M I^-. Which ion, I^- or Cl^- will precipitate first? Justify your answer with a calculation. K_{sp} for AgCl = 1.8×10^{-10}, K_{sp} for AgI = 8.5×10^{-17}.

To deal with this problem, calculate the $[Ag^+]$ required to cause precipitate formation for each salt. First, let's do AgCl:

	AgCl(s)	$\rightleftarrows$	Ag^+	+	Cl^-	At equilibrium:	K_{sp}	=	(x)(0.0100+x)
I	--		0		0.0100 M	Assume x << 0.0100		=	0.0100x
C	--		+x		+x		x	=	$K_{sp}/0.0100$
E	--		x		0.0100 +x		x	=	1.8×10^{-8}M

Repeat the calculation for AgI:

	AgI(s)	$\rightleftarrows$	Ag^+	+	I^-	At equilibrium:	K_{sp}	=	(x)(0.25+x)
I	--		0		0.25 M	Assume x << 0.25		=	0.25x
C	--		+x		+x		x	=	$K_{sp}/0.25$
E	--		x		0.25 +x		x	=	3.4×10^{-16}M

In both cases, our assumptions were reasonable. Since we defined x as $[Ag^+]$, our calculations tell us that AgI will precipitate once $[Ag^+]$ exceeds 3.4×10^{-16}M, but AgCl won't precipitate until $[Ag^+]$ exceed 1.8×10^{-8}M. **Therefore iodide ion, as AgI, will precipitate first.**

10. Consider a solution prepared by dissolving 0.10 mol of malonic acid and 0.20 mol of propionic acid in 1.00 L of solution. Malonic acid is a weak diprotic acid with $K_{a1} = 1.5 \times 10^{-3}$ and $K_{a2} = 2.0 \times 10^{-6}$, while propionic acid is a weak monoprotic acid with $K_a = 1.3 \times 10^{-5}$. Write enough valid equations to solve for the pH of this solution. You do not need to arrive at a numerical answer; you just need enough equations to solve for all of the unknowns.

Begin by writing all equilibria, with their associated equilibrium constant expressions. We'll abbreviate malonic acid as H_2A and propionic acid as HP.

$$\mathbf{H_2A} \rightleftarrows \mathbf{H^+} + \mathbf{HA^-} \qquad K_{a1} = \frac{[HA^-][H^+]}{[H_2A]}$$

$$HA^- \rightleftarrows H^+ + \mathbf{A^{2-}} \qquad K_{a2} = \frac{[A^{2-}][H^+]}{[HA^-]}$$

$$\mathbf{HP} \rightleftarrows H^+ + \mathbf{P^-} \qquad K_a = \frac{[P^-][H^+]}{[HP]}$$

$$H_2O \rightleftarrows H^+ + \mathbf{OH^-} \qquad K_w = [H^+][OH^-]$$

Seven unknowns (in bold), need seven equations. K expressions give us four, we need three more.

Charge balance: $[H^+] = [HA^-] + 2[A^{2-}] + [P^-] + [OH^-]$

Mass balance for malonic acid: $0.10 \text{ M} = [H_2A] + [HA^-] + [A^{2-}]$

Mass balance for propionic acid: $0.20 \text{ M} = [HP] + [P^-]$

In the space below, answer either problem 11 or problem 12. 15 points.

11. I've given you the task of preparing a pH 4.75 buffer. You've sought the help of a few of your classmates and have narrowed your choices down to the following list. Each of these combinations should produce a buffer with pH=4.75. Which student's suggestion would provide the best choice to make the highest capacity buffer? Justify your reasoning

Student	**Buffer Composition**	**K_a of weak acid**
Annie Yun	0.200M salicylic acid and 0.0032 M sodium salicylate	1.1×10^{-3}
Ty Trate	0.010 M acetic acid and 0.010 M sodium acetate	1.8×10^{-5}
Chris Talls	0.200 M acetic acid and 0.200 M sodium acetate	1.8×10^{-5}

For a buffer to have the best capacity, we would like the pK_a for the weak acid to be as close to the desired pH as possible, and we'd like a large concentration of both the weak acid and conjugate base to be present in the solution. The higher the concentration, the more strong acid or base can be absorbed without changing pH.

From the list above, Chris Talls recipe fits both requirements. Annie Yun suggests a combination which results in very dilute weak base because the pK_a is too far from the pH. Ty Trate has the ideal ratio of acid and conjugate base, but the dilute concentrations lead to poorer capacity that Chris' suggestion.

12. Your lab has synthesized a new weak, diprotic acid, that you have named *acidic* acid (creative!). The pK_{a1} for this acid is 4.26, while pK_{a2} is 11.08. What is the pH of a 0.100 M solution of acidic acid?

Looking at the K_a's, $K_{a1} = 5.50 \times 10^{-5}$ and $K_{a2} = 8.32 \times 10^{-12}$, indicating that the HA^- is a much weaker acid than H_2A, therefore it will not appreciably contribute to the pH of the solution. So, we can treat this as a weak monoprotic acid.

$$H_2A \rightleftarrows H^+ + A^-$$

Now we do the ICE thing:

	H_2A	$\rightleftarrows$	H^+	+	HA^-
I	0.100 M		0		0
C	-x		+x		+x
E	0.100-x		x		x

Inserting into the K_{a1} expression, we get:

$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} = \frac{x^2}{0.100 - x}$$

After some algebra, $0 = x^2 + K_{a1}x - 0.100K_{a1}$

Solving for x, we get $x = [H^+] = [HA^-] =$ **0.00231_7 M**, **pH = 2.64**.

We need to verify that ignoring K_{a2} was OK, or that $[A^{2-}] << [HA^-]$

$[A^{2-}] = K_{a2} \times [HA^-]/[H^+] = (8.32\times10^{-12})(0.00231M)/(0.00231M) = 8.32 \times 10^{-12}$ M, which is much less than 0.00231 M, so ignoring K_{a2} is OK.

(NOTE, since K_{a1} isn't extremely small, assuming $x << 0.100$ is probably a bad idea.)

Possibly Useful Information

$R = 8.31441\ \mathrm{J\ mol^{-1}\ K^{-1}}$

$^{o}C = K - 273.15$

$\Delta G = \Delta H - T\Delta S$

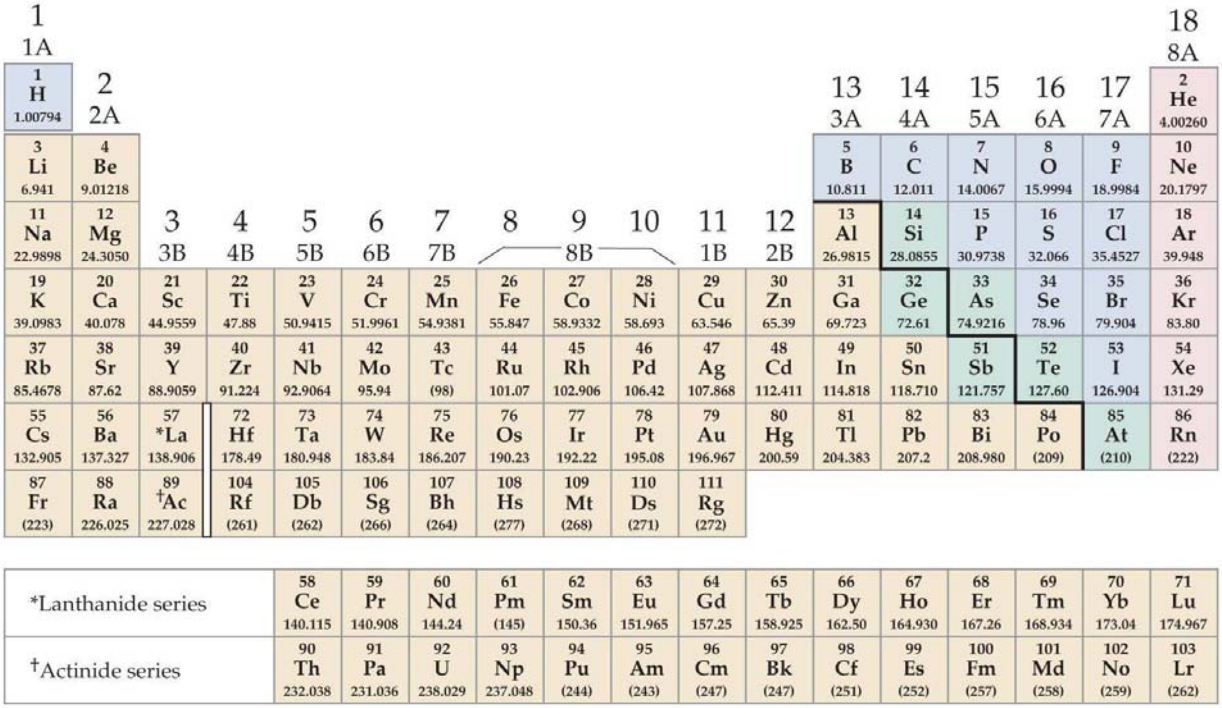
$\Delta G = \Delta G^{o} - RT\ln Q$

$pH + pOH = 14$

$K_aK_b = K_w$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$pH = pK_a + \log\left(\frac{[\text{conjugate base}]}{[\text{weak acid}]}\right)$$



1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.00794																	2 **He** 4.00260
3 **Li** 6.941	4 **Be** 9.01218											5 **B** 10.811	6 **C** 12.011	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.9984	10 **Ne** 20.1797
11 **Na** 22.9898	12 **Mg** 24.3050											13 **Al** 26.9815	14 **Si** 28.0855	15 **P** 30.9738	16 **S** 32.066	17 **Cl** 35.4527	18 **Ar** 39.948
19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.9559	22 **Ti** 47.88	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.9381	26 **Fe** 55.847	27 **Co** 58.9332	28 **Ni** 58.693	29 **Cu** 63.546	30 **Zn** 65.39	31 **Ga** 69.723	32 **Ge** 72.61	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9059	40 **Zr** 91.224	41 **Nb** 92.9064	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.07	45 **Rh** 102.906	46 **Pd** 106.42	47 **Ag** 107.868	48 **Cd** 112.411	49 **In** 114.818	50 **Sn** 118.710	51 **Sb** 121.757	52 **Te** 127.60	53 **I** 126.904	54 **Xe** 131.29
55 **Cs** 132.905	56 **Ba** 137.327	57 ***La** 138.906	72 **Hf** 178.49	73 **Ta** 180.948	74 **W** 183.84	75 **Re** 186.207	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.967	80 **Hg** 200.59	81 **Tl** 204.383	82 **Pb** 207.2	83 **Bi** 208.980	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.025	89 **†Ac** 227.028	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (271)	111 **Rg** (272)							

*Lanthanide series	58 **Ce** 140.115	59 **Pr** 140.908	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.36	63 **Eu** 151.965	64 **Gd** 157.25	65 **Tb** 158.925	66 **Dy** 162.50	67 **Ho** 164.930	68 **Er** 167.26	69 **Tm** 168.934	70 **Yb** 173.04	71 **Lu** 174.967
†Actinide series	90 **Th** 232.038	91 **Pa** 231.036	92 **U** 238.029	93 **Np** 237.048	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

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