Exam 5, Part II **Name(s) ____**

CHEM 222, Spring 2017 **Due by 11:59 PM, March. 22, 2017**

25 Points

You may complete the following individually, or with one (1) partner. You may use your textbook and notes, but may not receive assistance from your classmates or anyone other than Dr. Lamp. *<u>This signed sheet must accompany the completed assignment</u>*. By signing below, you certify that you completed the problems in accordance with these rules. No credit will be given to unsigned papers. You may ignore activities in these problems.

Signature(s)____ Date________________

1. Consider a saturated aqueous solution of lanthanum oxalate ($La_2(C_2O_4)_3$). Write mass and charge balance equations that describe this system. *Include all equilibria operating in the solution*. (Subtle hint: Oxalate is the conjugate base of a weak acid.) (6 points)

Below are the equilibria I was expecting you to include.

$La_2(C_2O_4)_3\ (s) \rightleftharpoons 2La^{3+} + 3C_2O_4^{2-}$	K_{sp}
$H_2C_2O_4 \rightleftharpoons HC_2O_4^{-} + H^{+}$	K_{a1}
$HC_2O_4^{-} \rightleftharpoons C_2O_4^{2-} + H^{+}$	K_{a2}
$H_2O \rightleftharpoons OH^{-} + H^{+}$	K_w

<u>Charge Balance:</u>

$$\mathbf{3[La^{+}] + [H^{+}] = [OH^{-}] + [HC_2O_4^{-}] + 2[C_2O_4^{2-}]}$$

<u>Mass Balance</u>:

We know that the total lanthanum concentration and total "oxalate" concentration must be related through the lanthanum oxalate reaction stoichiometry

$$3[La]_{Total} = 2[C_2O_4]_{Total}$$

$$\mathbf{3[La^{3+}] = 2([H_2C_2O_4] + [HC_2O_4^{-}] + [C_2O_4^{2-}])}$$

2. Consider an aqueous solution that is saturated with lead iodide and lead sulfate and also contains 0.10M Li_2SO_4 (a strong electrolyte). Write mass and charge balance equations that describe this system. *Include all equilibria operating in the solution*. (6 points)

Below are the equilibria and reactions I was expecting you to include.

$PbI_2(s) \rightleftharpoons Pb^{2+} + 2I^-$	K_{sp}
$PbSO_4\ (s) \rightleftharpoons Pb^{2+} + SO_4^{2-}$	K_{sp}
$Li_2SO_4 \rightarrow 2Li^+ + SO_4^{2-}$	
$SO_4^{2-} + H_2O \rightleftharpoons HSO_4^- + OH^-$	K_b
$H_2O \rightleftharpoons OH^- + H^+$	K_w

<u>Charge Balance</u>:

$$\mathbf{2[Pb^{2+}] + [Li^+] + [H^+] = [OH^-] + [I^-] + 2[SO_4^{2-}] + [HSO_4^-]}$$

<u>Mass Balance:</u>

We can easily write mass balance expressions for lithium ion because it is a spectator ion.

$$[Li]_{Total} = [Li]_{Li2SO4}$$
$$\mathbf{[Li^+] = 0.20\ M}$$

We know that the total lead concentration depends on both the lead iodide dissociation and on the lead sufate dissociation. We also know that sulfate can come from one of two sources, either lithium sulfate or lead sulfate. The combination of these two facts will help us arrive at a mass balance that relates lead, sulfate, and iodide.

$$[Pb]_{Total} = [Pb]_{PbI2} + [Pb]_{PbSO4}$$

Since the only form that lead exists in in solution is Pb^{2+}, $[Pb]_{Total} = [Pb^{2+}]$, so

$$[Pb^{2+}] = [Pb]_{PbI2} + [Pb]_{PbSO4}$$

$$[SO_4]_{Total} = [SO_4]_{PbSO4} + [SO_4]_{Li2SO4}$$

Since sulfate may exist in solution as SO_4^{2-} or HSO_4^- , $[SO_4]_{Total} = [HSO_4^-] + [SO_4^{2-}]$:

$$[HSO_4^-] + [SO_4^{2-}] = [SO_4]_{PbSO4} + [SO_4]_{Li2SO4}$$

We know that the only source of iodine in solution is PbI_2, and when PbI_2 dissociates, two iodides are produced per lead ion: $[Pb]_{PbI2} = ½ [I^-]$

We also know that every time a lead sulfate dissociates, one lead ion is produced for each sulfate ion: $[Pb]_{PbSO4} = [SO_4]_{PbSO4.}$ Also, we know that lithium sulfate is a strong electrolyte, so the sulfate it produces is determined by its formality: $[SO_4]_{LiSO4} = 0.10$ M

Pulling it all together:

$$[HSO_4^-] + [SO_4^{2-}] = [Pb]_{PbSO4} + 0.10\ M$$
$$[Pb]_{PbSO4} = [HSO_4^-] + [SO_4^{2-}] - 0.10\ M$$
$$\mathbf{[Pb^{2+}] = ½\ [I^-] + [HSO_4^-] + [SO_4^{2-}] - 0.10\ M}$$

3. You have prepared a solution by dissolving 0.20 mol glutaric acid ($C_5H_8O_2$, $pK_{a1} = 4.34$, $pK_{a2} = 5.42$) and 0.10 mol mandelic acid ($C_8H_8O_3$, $pK_a = 3.86$) in 1.00 L of water. Write all equilibria occurring in solution as well as mass balance and charge balance expressions for this system. Determine the pH of this solution. You may make *valid* simplifying assumptions, use spreadsheets, or solve the system directly. If you use a computer to solve the system, be sure to attach a printout of the computer output. (13 points)

Let's call glutaric acid H_2G and mandelic acid HM.

$HM \rightleftharpoons M^- + H^+$	$K_a = 10^{-3.86} = [M^-][H^+]/[HM]$
$H_2G \rightleftharpoons HG^- + H^+$	$K_{a1} = 10^{-4.34} = [HG^-][H^+]/[H_2G]$
$HG^- \rightleftharpoons G^{2-} + H^+$	$K_{a2} = 10^{-5.42} = [g^{2-}][H^+]/[HG^-]$
$H_2O \rightleftharpoons OH^- + H^+$	$K_w = [H^+][OH^-]$

Charge Balance: $\mathbf{[H^+] = [OH^-] + [HG^-] + 2[G^{2-}] + [M^-]}$

Mass Balance for mandelic acid: $[M]_{Total} = 0.10\ M = [HM] + [M^-]$
Mass Balance for glutaric acid: $[G]_{Total} = 0.20\ M = [H_2G] + [HG^-] + [G^{2-}]$

One strategy is to get everything ultimately in terms of $[H^+]$ so that we can "guess" and $[H^+]$ and solve the problem iteratively.

$$\mathbf{[OH^-] = K_w/[H^+]}$$

Working with HM:

$$\mathbf{[M^-] = 0.10 - [HM]} \text{ and } K_a = [M^-][H^+]/[HM], \text{ so}$$
$$K_a = (0.10 - [HM])[H^+]/[HM]$$

Rearranging:

$$[HM]K_a = 0.10[H^+] - [HM][H^+]$$
$$[HM]K_a + [HM][H^+] = 0.10[H^+]$$
$$[HM](K_a + [H^+]) = 0.10[H^+]$$
$$\mathbf{[HM] = 0.10[H^+]/(K_a + [H^+])}$$

Similarly with H_2G:

$$0.20\ M = [H_2G] + [HG^-] + [G^{2-}]$$

From the K_a expressions:

$$\mathbf{[H_2G] = [HG^-][H^+]/K_{a1}} \text{ and } \mathbf{[G^{2-}] = K_{a2}[HG^-]/[H^+]}$$

So

$$0.20\ M = ([HG^-][H^+]/K_{a1}) + [HG^-] + (K_{a2}[HG^-]/[H^+])$$

Rearranging:

$$0.20\ M = [HG^-]\{([H^+]/K_{a1}) + 1 + (K_{a2}/[H^+])\}$$
$$\mathbf{[HG^-] = 0.20/\{([H^+]/K_{a1}) + 1 + (K_{a2}/[H^+])\}}$$

Now, we can "guess" a concentration of H^+ and calculate concentrations of HG^-, H_2G, G^{2-}, HM, M^{2-} and OH^- and use the charge balance expression to determine if we have reached the correct solution. Lather, rinse, repeat and iterate until we have arrived at a solution. You may also use something like Solver in Excel to arrive at a solution.

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1				pH	$[H^+]$	$[OH^-]$	$[HG^-]$	$[H_2G]$	$[G^{2-}]$	[HM]	$[M^-]$		Charge	
2	K_{a1}	4.5709E-05		1	0.1	1E-13	9.14E-05	0.199909	3.474E-09	0.099862	0.000138		0.099771	
3	K_{a2}	3.8019E-06		2	0.01	1E-12	0.00091	0.19909	3.4598E-07	0.098638	0.001362		0.007728	
4				3	0.001	1E-11	0.008741	0.191226	3.3231E-05	0.08787	0.01213		-0.01994	
5	K_a	1.3804E-04		2.5	0.003162	3.16E-12	0.00285	0.197147	3.426E-06	0.095817	0.004183		-0.00388	
6				2.2	0.00631	1.58E-12	0.001438	0.198561	8.6675E-07	0.097859	0.002141		0.002728	
7	[G]	0.2		2.4	0.003981	2.51E-12	0.00227	0.197728	2.168E-06	0.096649	0.003351		-0.00164	
8	[M]	0.1		2.3	0.005012	2E-12	0.001808	0.198191	1.3711E-06	0.09732	0.00268		0.000521	
9				2.35	0.004467	2.24E-12	0.002026	0.197972	1.7243E-06	0.097002	0.002998		-0.00056	
10				2.34	0.004571	2.19E-12	0.00198	0.198018	1.647E-06	0.097069	0.002931		-0.00034	
11				2.33	0.004677	2.14E-12	0.001936	0.198063	1.5733E-06	0.097133	0.002867		-0.00013	
12				2.32	0.004786	2.09E-12	0.001892	0.198107	1.5028E-06	0.097197	0.002803		8.82E-05	
13				2.325	0.004732	2.11E-12	0.001914	0.198085	1.5376E-06	0.097165	0.002835		-2E-05	
14				2.322	0.004764	2.1E-12	0.001901	0.198098	1.5166E-06	0.097184	0.002816		4.5E-05	
15				2.324	0.004742	2.11E-12	0.001909	0.198089	1.5306E-06	0.097172	0.002828		1.73E-06	
16				2.3245	0.004737	2.11E-12	0.001911	0.198087	1.5341E-06	0.097168	0.002832		-9.1E-06	
17				2.3241	0.004741	2.11E-12	0.00191	0.198089	1.5313E-06	0.097171	0.002829		-4.4E-07	
18				2.324	0.004742	2.11E-12	0.001909	0.198089	1.5306E-06	0.097172	0.002828		1.73E-06	
19														
20														
21														
22			Solver	2.32408	0.004742	2.11E-12	0.00191	0.198089	1.5312E-06	0.097171	0.002829		0	
23														
24			pH											
25			$[H^+]$	`=10^-D2`										
26			$[OH^-]$	`=0.00000000000001/E2`										
27			$[HM^-]$	`=$B$7/((E2/$B$2)+1+($B$3/E2))`										
28			$[H_2M]$	`=+G2*E2/$B$2`										
29			$[M^{2-}]$	`=+$B$3*G2/E2`										
30			[HP]	`=+($B$8*E2)/($B$5+E2)`										
31			$[P^-]$	`=$B$8-J2`										
32			Charge	`=+E2-(F2+G2+2*I2+K2)`										

After iteration, pH = 2.324