Exam 5, Part II **Name(s) _____**
CHEM 222, Spring 2021 **Due *in class*, March 22, 2021**
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. *This signed sheet must accompany the completed assignment*. By signing below, you certify that you completed the problems in accordance with these rules. No credit will be given to unsigned papers.

Signature(s)_____ Date_____

1. Consider a saturated aqueous solution of silver phosphate (Ag_3PO_4). Write the pertinent reactions and derive mass and charge balance equations that describe this system. *Include all acid-base equilibria involving phosphate, but ignore any acid-base equilibria involving silver*. (Subtle hint: Phosphate is the conjugate base of a weak acid.) (6 points)

   Below are the equilibria I was expecting you to include. You could also include the silver hydroxide complexation and precipitation equilibria, but I wasn't expecting you to hunt them down.

   $Ag_3PO_4\,(s) \rightleftharpoons 3Ag^+ + PO_4^{3-}$ K_{sp}
   $H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$ K_{a1}
   $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$ K_{a2}
   $HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$ K_{a3}
   $H_2O \rightleftharpoons OH^- + H^+$ K_w

   Charge Balance:

   $$\mathbf{[Ag^+] + [H^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]}$$

   Mass Balance:
   We know that the total silver concentration and total "phosphate" concentration must be related through the silver phosphate reaction stoichiometry

   $$[Ag]_{Total} = 3[PO_4]_{Total}$$
   $$\mathbf{[Ag^+] = 3([H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}])}$$

2. Consider an aqueous solution that is saturated with silver chloride and silver chromate and also contains 0.20M Na_2CrO_4 and 0.10 M $NaNO_3$ (both strong electrolytes). Write the pertinent reactions and derive mass and charge balance equations that describe this system. *Ignore any acid-base equilibria involving silver*. (6 points)

Below are the equilibria and reactions I was expecting you to include. You could also include the chromate acid/base chemistry, but I wasn't expecting you to hunt that down.

$$Ag_2CrO_4\ (s) \rightleftharpoons 2Ag^+ + CrO_4^{2-} \qquad K_{sp}$$
$$Ag_2Cl\ (s) \rightleftharpoons Ag^+ + Cl^- \qquad K_{a1}$$
$$Na_2CrO_4 \rightarrow 2Na^+ + CrO_4^{2-}$$
$$NaNO_3 \rightarrow Na^+ + NO_3^-$$
$$H_2O \rightleftharpoons OH^- + H^+ \qquad K_w$$

Charge Balance:

$$\mathbf{[Na^+] + [Ag^+] + [H^+] = [OH^-] + [Cl^-] + 2[CrO_4^{2-}] + [NO_3^-]}$$

Mass Balance:

We can easily write mass balance expressions for sodium and nitrate ions because there are spectator ions.

$$[Na]_{Total} = [Na]_{Na2CrO4} + [Na]_{NO3} = 2(0.20M) + 0.10M$$
$$\mathbf{[Na^+] = 0.50\ M}$$
$$\mathbf{[NO_3^-] = 0.10\ M}$$

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

$$[Ag]_{Total} = [Ag]_{Ag2CrO4} + [Ag]_{AgCl}$$
$$[CrO_4]_{Total} = [CrO_4]_{Na2CrO4} + [CrO_4]_{Ag2CrO4}$$

But, $[Ag]_{Ag2CrO4} = 2[CrO_4]_{Ag2CrO4}$
and $[Ag]_{AgCl} = [Cl^-]$
and $[CrO_4]_{Na2CrO4} = 0.20$ M

So $[Ag^+] = 2[CrO_4]_{Ag2CrO4} + [Cl^-]$, or $[CrO_4]_{Ag2CrO4} = ½\ ([Ag^+] - [Cl^-])$ and

$$\mathbf{[CrO_4^{2-}] = 0.20\ M + ½\ ([Ag^+] - [Cl^-])}$$

3. You have prepared a solution by dissolving 0.20 mol adipic acid ($C_6H_{10}O_4$, $pK_{a1} = 4.42$, $pK_{a2} = 5.42$) and 0.10 mol benzoic acid ($C_6H_6O_2$, $pK_a = 4.20$) 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 (which I encourage), be sure to either upload a copy of the spreadsheet, share any Google sheets, or include a printout of the computer output. (13 points)

Let's call maleic acid H_2A and pyruvic acid HB.

$HB \rightleftharpoons B^- + H^+$	$K_a = 10^{-2.48} = [B^-][H^+]/[HB]$
$H_2A \rightleftharpoons HA^- + H^+$	$K_{a1} = 10^{-1.92} = [HA^-][H^+]/[H_2A]$
$HA^- \rightleftharpoons A^{2-} + H^+$	$K_{a2} = 10^{-6.27} = [A^{2-}][H^+]/[HA^-]$
$H_2O \rightleftharpoons OH^- + H^+$	$K_w = [H^+][OH^-]$

Charge Balance: $\mathbf{[H^+] = [OH^-] + [HA^-] + 2[A^{2-}] + [B^-]}$

Mass Balance for pyruvic acid: $[B]_{Total} = 0.15\ M = [HB] + [B^-]$
Mass Balance for maleic acid: $[A]_{Total} = 0.25\ M = [H_2A] + [HA^-] + [A^{2-}]$

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 HB:

$\mathbf{[B^-] = 0.10 - [HB]}$ and $K_a = [B^-][H^+]/[HB]$, so

$$K_a = (0.10 - [HB])[H^+]/[HB]$$

Rearranging:

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

Similarly with H_2A:

$$0.20\ M = [H_2A] + [HA^-] + [A^{2-}]$$

From the K_a expressions:

$\mathbf{[H_2A] = [HA^-][H^+]/K_{a1}}$ and $\mathbf{[A^{2-}] = K_{a2}[HA^-]/[H^+]}$

So

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

Rearranging:

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

Now, we can "guess" a concentration of H^+ and calculate concentrations of HA^-, H_2A, A^{2-}, HB, B^{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.

	A	B	C	D	E	F	G	H	I	J	K	L	M
1				pH	$[H^+]$	$[OH^-]$	$[HA^-]$	$[H_2A]$	$[A^{2-}]$	[HB]	$[B^-]$		Charge
2	K_{a1}	3.8019E-05		2	0.01	1E-12	0.000757	0.199242	2.8799E-07	0.099373	0.000627		0.008615
3	K_{a2}	3.8019E-06		3	0.001	1E-11	0.007324	0.192648	2.7846E-05	0.094065	0.005935		-0.01232
4				2.5	0.003162	3.16E-12	0.002376	0.197621	2.8565E-06	0.098044	0.001956		-0.00118
5	K_a	6.3096E-05		2.4	0.003981	2.51E-12	0.001892	0.198106	1.8068E-06	0.09844	0.00156		0.000525
6				2.45	0.003548	2.82E-12	0.00212	0.197877	2.2719E-06	0.098253	0.001747		-0.00032
7	[A]	0.2		2.42	0.003802	2.63E-12	0.00198	0.198018	1.9802E-06	0.098368	0.001632		0.000185
8	[B]	0.1		2.43	0.003715	2.69E-12	0.002026	0.197972	2.073E-06	0.09833	0.00167		1.55E-05
9				2.44	0.003631	2.75E-12	0.002073	0.197925	2.1702E-06	0.098292	0.001708		-0.00015
10				2.435	0.003673	2.72E-12	0.002049	0.197949	2.1211E-06	0.098311	0.001689		-6.9E-05
11				2.432	0.003698	2.7E-12	0.002035	0.197963	2.0921E-06	0.098323	0.001677		-1.8E-05
12				2.431	0.003707	2.7E-12	0.00203	0.197967	2.0825E-06	0.098326	0.001674		-1.5E-06
13				2.43	0.003715	2.69E-12	0.002026	0.197972	2.073E-06	0.09833	0.00167		1.55E-05
14				2.4305	0.003711	2.69E-12	0.002028	0.19797	2.0778E-06	0.098328	0.001672		7E-06
15				2.4308	0.003709	2.7E-12	0.00203	0.197968	2.0806E-06	0.098327	0.001673		1.91E-06
16				2.4309	0.003708	2.7E-12	0.00203	0.197968	2.0816E-06	0.098327	0.001673		2.12E-07
17				2.43095	0.003707	2.7E-12	0.00203	0.197968	2.0821E-06	0.098327	0.001673		-6.4E-07
18													
19													
20													
21													
22			Solver	2.430913	0.003708	2.7E-12	0.00203	0.197968	2.0817E-06	0.098327	0.001673		0
23													
24			pH										
25			$[H^+]$	=10^-D2									
26			$[OH^-]$	=0.00000000000001/E2									
27			$[HA^-]$	=$B$7/((E2/$B$2)+1+($B$3/E2))									
28			$[H_2A]$	=+G2*E2/$B$2									
29			$[A^{2-}]$	=+$B$3*G2/E2									
30			[HB]	=+($B$8*E2)/($B$5+E2)									
31			$[B^-]$	=$B$8-J2									
32			Charge	=+E2-(F2+G2+2*I2+K2)									
33													

After iteration, we find tha pH = 2.43