Exam 5, Part II

(1) $Ag_3PO_{4(s)} \rightleftharpoons 3Ag^+ + PO_4^{3-}$ $\quad K_{sp} = [Ag^+]^3[PO_4^{3-}]$

$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$ $\quad K_{b1} = \frac{[HPO_4^{2-}][OH^-]}{[PO_4^{3-}]}$

$HPO_4^- + H_2O \rightleftharpoons H_2PO_4^- + OH^-$ $\quad K_{b2} = \frac{[H_2PO_4^-][OH^-]}{[HPO_4^{2-}]}$

$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$ $\quad K_{b3} = \frac{[H_3PO_4][OH^-]}{[H_2PO_4^-]}$

$H_2O \rightleftharpoons H^+ + OH^-$ $\quad K_w = [H^+][OH^-]$

<u>Charge balance:</u>

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

<u>Mass Balance:</u>

$$[Ag^+]_T = 3[PO_4]_T$$

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

7 equations, 7 unknowns ✓

(2.)

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^- \qquad K_{sp} = [Ag^+][Cl^-]$$

$$Ag_2CrO_{4\,(s)} \rightleftharpoons 2Ag^+ + CrO_4^{2-} \qquad K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$Na_2CrO_4 \longrightarrow 2Na^+ + CrO_4^{2-}$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_w = [H^+][OH^-]$$

Charge Balance:

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

Mass Balance

$$[Na^+] = 2(0.20\,M) = 0.40\,M$$

$$[Ag]_T = [Cl^-]_T + 2[CrO_4^{2-}]_{Ag_2CrO_4} - [CrO_4^{2-}]_{Na_2CrO_4}$$

$$\therefore [Ag^+] = [Cl^-] + 2[CrO_4^{2-}] - 0.20\,M$$

6 equations, 6 unknowns.

(3) Maleic acid = H_2M , Pyruvic acid = HPy

$$H_2M \rightleftharpoons H^+ + HM^- \qquad K_{a_1} = \frac{[H^+][HM^-]}{[H_2M]} = 10^{-1.92}$$

$$HM^- \rightleftharpoons H^+ + M^{2-} \qquad K_{a_2} = \frac{[H^+][M^{2-}]}{[HM^-]} = 10^{-6.27}$$

$$HPy \rightleftharpoons H^+ + Py^- \qquad K_{Py} = \frac{[H^+][Py^-]}{[HPy]} = 10^{-2.48}$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_w = [H^+][OH^-]$$

Charge Balance

$$[H^+] = [HM^-] + 2[M^{2-}] + [Py^-] + [OH^-]$$

Mass Balance

$$[M]_T = 0.20M = [H_2M] + [HM^-] + [M^{2-}]$$

$$[Py]_T = 0.10\,M = [HPy] + [Py^-]$$

~~7~~ 6 equations, 7 unknowns

(A) Numerical Solution: get things in terms of $[H^+]$, "guess" $[H^+]$, then iterate.

$$K_{Py} = \frac{[H^+][Py^-]}{[HPy]} = \frac{[H^+][Py^-]}{0.1-[Py^-]}$$

$$\text{so: } [Py^-] = \frac{0.1\,K_{Py}}{[H^+] + K_{Py}} \qquad *$$

$$[HPy] = 0.1 - [Py^-] \qquad *$$

3 cont'd

from mass balance

$$0.2M = [H_2M] + [HM^-] + [M^{2-}]$$

from Ka_1: $[HM^-] = \frac{[H_2M]Ka_1}{[H^+]}$ *

from Ka_2: $[M^{2-}] = \frac{[HM^-]Ka_2}{[H^+]} = \frac{[H_2M]Ka_1Ka_2}{[H^+]^2}$ *

$$\therefore 0.2M = [H_2M] + \frac{[H_2M]Ka_1}{[H^+]} + \frac{[H_2M]Ka_1Ka_2}{[H^+]^2}$$

solving for $[H_2M]$: $[H_2M] = \frac{0.2M}{1 + Ka_1/[H^+] + Ka_1Ka_2/[H^+]^2}$ *

$[OH^-] = Kw/[H^+]$ *

so, now we can iterate by changing $[H^+]$ + solving for other terms until charge balance is satisfied $\Rightarrow [H^+] - ([HM^-] + 2[M^{2-}] + [P_y^-] + [OH^-]) = 0$

Spreadsheet is attached

$[H^+] = 0.04718M$, $pH = 1.32_6$

4a

	A	B	C	D	E	F	G	H	I
1									
2	**ka1**	**0.012022644**							
3	**Ka2**	**5.37032E-07**							
4	**Kp**	**0.003311311**							
5									
6	**pH**	**$[H^+]$**	**$[OH^-]$**	**$[H_2M]$**	**$[HM^-]$**	**$[M^{2-}]$**	**$[P^-]$**	**[HP]**	**Charge**
7	2	0.01	1E-12	0.09081	0.10918	5.8634E-06	0.02488	0.07512	-0.1241
8	3	0.001	1E-11	0.01535	0.18455	9.9110E-05	0.07681	0.02319	-0.2606
9	4	0.0001	1E-10	0.00164	0.19730	1.0596E-03	0.09707	0.00293	-0.2964
10	5	0.00001	0.000000001	0.00016	0.18966	1.0185E-02	0.09970	0.00030	-0.3097
11	6	0.000001	0.00000001	0.00001	0.13011	6.9875E-02	0.09997	0.00003	-0.3698
12	7	0.0000001	0.0000001	0.00000	0.03140	1.6860E-01	0.10000	0.00000	-0.4686
13	8	0.00000001	0.000001	0.00000	0.00366	1.9634E-01	0.10000	0.00000	-0.4963
14	9	0.000000001	0.00001	0.00000	0.00037	1.9963E-01	0.10000	0.00000	-0.4996
15	10	1E-10	0.0001	0.00000	0.00004	1.9996E-01	0.10000	0.00000	-0.5001
16	0	1	1E-14	0.19762	0.00238	1.2760E-09	0.00033	0.09967	0.9973
17	1	0.1	1E-13	0.17854	0.02146	1.1527E-07	0.00321	0.09679	0.0753
18	1.1	0.079432823	1.25893E-13	0.17371	0.02629	1.7775E-07	0.00400	0.09600	0.0491
19	1.3	0.050118723	1.99526E-13	0.16131	0.03869	4.1462E-07	0.00620	0.09380	0.0052
20	1.5	0.031622777	3.16228E-13	0.14491	0.05509	9.3560E-07	0.00948	0.09052	-0.0329
21	1.4	0.039810717	2.51189E-13	0.15361	0.04639	6.2578E-07	0.00768	0.09232	-0.0143
22	1.35	0.044668359	2.23872E-13	0.15758	0.04241	5.0993E-07	0.00690	0.09310	-0.0046
23	1.32	0.047863009	2.0893E-13	0.15985	0.04015	4.5051E-07	0.00647	0.09353	0.0012
24	1.33	0.046773514	2.13796E-13	0.15910	0.04090	4.6955E-07	0.00661	0.09339	-0.0007
25	1.325	0.047315126	2.11349E-13	0.15948	0.04052	4.5994E-07	0.00654	0.09346	0.0003
26	1.327	0.047097733	2.12324E-13	0.15933	0.04067	4.6376E-07	0.00657	0.09343	-0.0001
27									
28	**Solver**								
29	1.32627	0.04718	2.11968E-13	0.15938	0.04062	4.6236E-07	0.00656	0.09344	-2.88E-10
30									
31	**$[H^+]$**	B7 =10^-A7				**$[P^-]$**	G7 = (0.1*$B$4)/(B7+$B$4)		
32	**$[OH^-]$**	C7 = 0.00000000000001/B7				**[HP]**	H7 = 0.1-G7		
33	**$[H_2M]$**	D7 = 0.2/(1+($B$2/B7)+($B$2*$B$3/B7^2))				**Charge**	I7 = B7-(E7+2*F7+G7+C7)		
34	**$[HM^-]$**	E7 = D7*$B$2/B7							
35	**$[M^{2-}]$**	F7 = $B$3*E7/B7							

Simplifying assumptions:

Since $K_{a_1} \approx K_{py} \gg K_{a_2} \gg K_w$

K_{a_2} + K_w equilibria don't go very far

∴ assume

$[HM^-] > [Py^-] \gg [M^{2-}] \gg [OH^-]$

Charge Balance becomes: $[H^+] = [HM^-] + [Py^-]$

Mass Balance becomes: $0.20 = [H_2M] + [HM^-]$

$0.10 = [HPy] + [Py^-]$

from K_{py}: $K_{py} = \frac{[H^+][Py^-]}{0.1 - [Py^-]} = \frac{[H^+]([H^+] - [HM^-])}{0.1 - [H^+] + [HM^-]}$

So, $0.1 K_{py} - [H^+]K_{py} + K_{py}[HM^-] = [H^+]^2 - [H^+][HM^-]$

$[HM^-] = \frac{[H^+]^2 + [H^+]K_{py} - 0.1 K_{py}}{K_{py} + [H^+]}$

from K_{a_1}: $K_{a_1} = \frac{[H^+][HM^-]}{[H_2M]} = \frac{[H^+][HM^-]}{0.2 - [HM^-]}$

$0.2 K_{a_1} - [HM^-]K_{a_1} = [H^+][HM^-]$

$[HM^-] = \frac{0.2 K_{a_1}}{[H^+] + K_{a_1}}$

now we have a single equation in terms of $[H^+]$.
It's nonlinear, so we still need to take a numerical approach.

$$0 = \frac{[H^+]^2 + [H^+]K_{py} - 0.1 K_{py}}{K_{py} + [H^+]} - \frac{0.2 K_{a_1}}{[H^+] + K_{a_1}}$$

Solving numerically, $[H^+] = 0.0472$ M, pH = 1.326