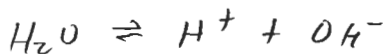
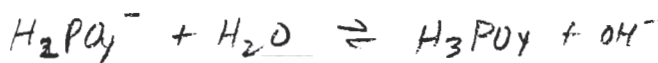
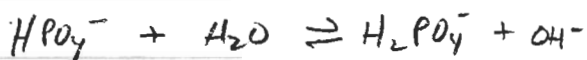
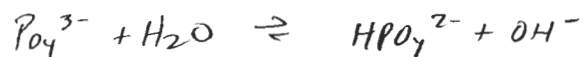
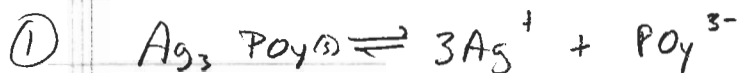


## Exan 5, Part II



$$K_{sp} = [\text{Ag}^+]^3 [\text{PO}_4^{3-}]$$

$$K_{b1} = \frac{[\text{HPO}_4^{2-}] [\text{OH}^-]}{[\text{PO}_4^{3-}]}$$

$$K_{b2} = \frac{[\text{H}_2\text{PO}_4^-] [\text{OH}^-]}{[\text{HPO}_4^{2-}]}$$

$$K_{b3} = \frac{[\text{H}_3\text{PO}_4] [\text{OH}^-]}{[\text{H}_2\text{PO}_4^-]}$$

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

Charge balance:

$$[\text{H}^+] + [\text{Ag}^+] = 3[\text{PO}_4^{3-}] + 2[\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{OH}^-]$$

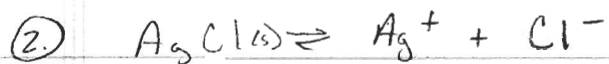
Mass Balance:

$$[\text{Ag}^+]_T = 3[\text{PO}_4]_T$$

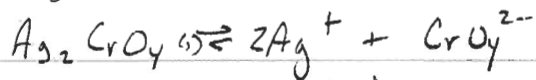
$$[\text{Ag}^+] = 3([\text{PO}_4^{3-}] + [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{H}_3\text{PO}_4])$$

7 equations, 7 unknowns  $\checkmark$

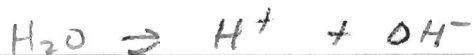
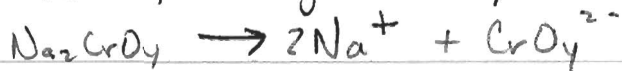
(2)



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$



$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$



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

Charge Balance:

$$[\text{Ag}^+] + [\text{Na}^+] + [\text{H}^+] = [\text{Cl}^-] + 2[\text{CrO}_4^{2-}] + [\text{OH}^-]$$

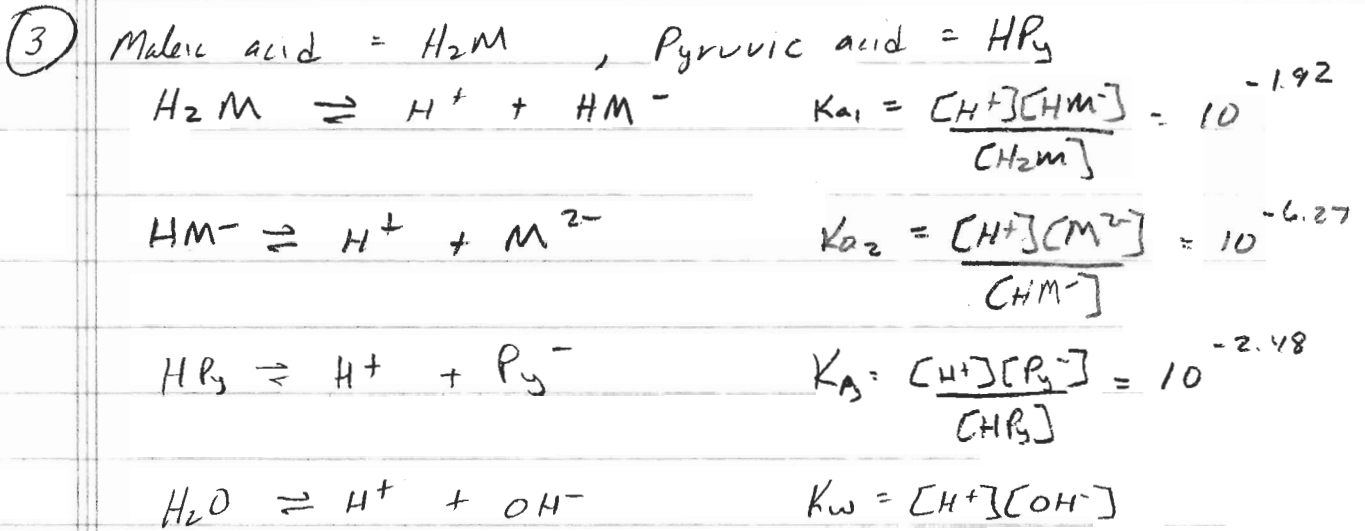
Mass Balance

$$[\text{Na}^+] = 2(0.20\text{M}) = 0.40\text{M}$$

$$[\text{Ag}]_T = [\text{Cl}]_T + 2[\text{CrO}_4^{2-}]_{\text{Ag}_2\text{CrO}_4} - [\text{CrO}_4^{2-}]_{\text{Na}_2\text{CrO}_4}$$

$$\therefore [\text{Ag}^+] = [\text{Cl}^-] + 2[\text{CrO}_4^{2-}] - 0.20\text{M}$$

6 equations, 6 unknowns.



Charge Balance

$$[H^+] = [HM^-] + 2[M^{2-}] + [P_3^-] + [OH^-]$$

Mass Balance

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

$$[P_3]_T = 0.10 M = [HP_3] + [P_3^-]$$

7 equations, 7 unknowns

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

$$K_{P_3} = \frac{[H^+][P_3^-]}{[HP_3]} = \frac{[H^+][P_3^-]}{0.1 - [P_3^-]}$$

$$\text{so: } [P_3^-] = \frac{0.1 K_{P_3}}{[H^+] + K_{P_3}} \quad *$$

$$[HP_3] = 0.1 - [P_3^-] \quad *$$

3 cont'd

from mass balance

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

from  $K_{a1}$ :  $[HM^-] = \frac{[H_2M]K_{a1}}{[H^+]}$  \*

from  $K_{a2}$ :  $[M^{2-}] = \frac{[HM^-]K_{a2}}{[H^+]} = \frac{[H_2M]K_{a1}K_{a2}}{[H^+]^2}$  \*

$$\therefore 0.2M = [H_2M] + \frac{[H_2M]K_{a1}}{[H^+]} + \frac{[H_2M]K_{a1}K_{a2}}{[H^+]^2}$$

solving for  $[H_2M]$ :  $[H_2M] = \frac{0.2M}{1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2}}$  \*

$$[OH^-] = K_w/[H^+]$$
 \*

so, now we can iterate by changing  $[H^+]$  +

solving for other terms until charge balance is satisfied  $\Rightarrow [H^+] - ([HM^-] + 2[M^{2-}] + [P_3^-] + [OH^-]) = 0$

\*spreadsheet is attached\*

$$[H^+] = 0.04718M, \text{ pH} = 1.326$$

	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 <sup>+</sup> ]	[OH]	[H <sub>2</sub> M]	[HM]	[M <sup>2</sup> ]	[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 <sup>+</sup> ]	B7 = 10^-A7				[P]	G7 = (0.1*\$B\$4)/(B7+\$B\$4)		
32	[OH]	C7 = 0.000000000000001/B7				[HP]	H7 = 0.1-G7		
33	[H <sub>2</sub> M]	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 <sup>2</sup> ]	F7 = \$B\$3*E7/B7							

Simplifying assumptions:

Since  $K_{a1} \approx K_{py} \gg K_{a2} \gg K_w$

$K_{a2}$  &  $K_w$  equilibria don't go very far

$\therefore$  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  $K_{a1}$ :  $K_{a1} = \frac{[H^+][HM^-]}{[H_2M]} = \frac{[H^+][HM^-]}{0.2 - [HM^-]}$

$$0.2 K_{a1} - [HM^-] K_{a1} = [H^+] [HM^-]$$

$$[HM^-] = \frac{0.2 K_{a1}}{[H^+] + K_{a1}}$$

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

$$0 = \frac{[H^+]^2 + [H^+] K_{py} - 0.1 K_{py}}{K_{py} + [H^+]} - \frac{0.2 K_{a1}}{[H^+] + K_{a1}}$$

Solving numerically,  $[H^+] = 0.0472 \text{ M}$ ,  $\text{pH} = 1.326$