When do the approximations fail?

$$[H^+] \approx \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}}$$ 9-11 8th, 11-11 6th

pH = ½ (pK_{a1} + pK_{a2}) 9-12 8th, 11-11 6th

Now let's consider the case where K_{a1} and K_{a2} are close to each other, and F is small.

Assume 1.0e-3 M NaHM

$HM^- = H^+ + M^{2-}$ K_{a2} = 8.9e-6

$HM^- + H^+ = H_2M$ K_{a1} = 4.0e-4

$$[H^+] \approx \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}}$$

$$= \sqrt{\frac{4.0\times10^{=4}\times8.9\times10^{-6}\times1.0\times10^{-3} + 4.0\times10^{-4}\times1.00\times10^{-14}}{4.0\times10^{-4} + 1.0\times10^{-3}}}$$

= 5.04e-5 pH = 4.297

Now consider the MBE for this reaction:

F = 1.0e-3 = $[H_2M]$ + $[HM^-]$ + $[M^{2-}]$

$[HM^-] = 1.0e\text{-}3 - [H_2M] - [M^{2-}]$

if $[H_2M]$ & $[M^{2-}]$ are significant we cannot make the assumption that

$[HM^-] = 1.0e\text{-}3 = F$

from $K_{a1} = [HM^-][H^+]/[H_2M]$

$4.0e\text{-}4 = 1.0e\text{-}3*5.04e\text{-}5/[H_2M]$

$[H_2M] = 1.26e\text{-}4$ M

$K_{a2} = [H^+][M^{2-}]/[HM^-]$

$8.9e\text{-}6 = 5.04e\text{-}5*[M^{2-}]/1.0e\text{-}3$

$[M^{2-}] = 1.77e\text{-}4$

Back to the MBE

$[HM^-] = F - [H_2M] - [M^{2-}] = 1.00e\text{-}3 - 1.26e\text{-}4$ M $- 1.77e\text{-}4$

$[HM^-] = 6.97e\text{-}4$

Now plug this back into

$$[H^+] \approx \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}}$$

$$= \sqrt{\frac{4.0\times10^{=4}\times8.9\times10^{-6}\times6.97\times10^{-4} + 4.0\times10^{-4}\times1.00\times10^{-14}}{4.0\times10^{-4} + 6.97\times10^{-4}}}$$

= 4.76e-5 M

we will find that

$[H_2M]$ = 8.29e-5 M

$[M^{2-}]$ = 1.30e-4 M

plug this back into the MBE

now $[HM^-]$ = 7.87e-4 M

repeat 3rd time $[HM^-]$ = 4.86e-5

4th time $[HM^-]$ = 4.83e-5

pH = 4.316

with the 5.04e-5 which we calculated before pH = 4.297

using pH = ½(pK_{a1} + pK_{a2}) = 4.224