

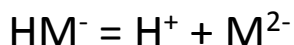
When do the approximations fail?

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

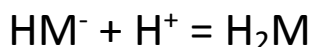
$$\text{pH} = \frac{1}{2} (\text{p}K_{a1} + \text{p}K_{a2}) \quad 9-12 \text{ 8}^{\text{th}}, 11-11 \text{ 6}^{\text{th}}$$

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

Assume $1.0 \times 10^{-3} \text{ M NaHM}$



$$K_{a2} = 8.9 \times 10^{-6}$$



$$K_{a1} = 4.0 \times 10^{-4}$$

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

$$= \sqrt{\frac{4.0 \times 10^{-4} \times 8.9 \times 10^{-6} \times 1.0 \times 10^{-3} + 4.0 \times 10^{-4} \times 1.00 \times 10^{-14}}{4.0 \times 10^{-4} + 1.0 \times 10^{-3}}}$$

$$= 5.04 \times 10^{-5} \quad \text{pH} = 4.297$$

Now consider the MBE for this reaction:

$$F = 1.0 \times 10^{-3} = [\text{H}_2\text{M}] + [\text{HM}^-] + [\text{M}^{2-}]$$

$$[\text{HM}^-] = 1.0\text{e-}3 - [\text{H}_2\text{M}] - [\text{M}^{2-}]$$

if $[\text{H}_2\text{M}]$ & $[\text{M}^{2-}]$ are significant we cannot make the assumption that

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

from $K_{a1} = [\text{HM}^-][\text{H}^+]/[\text{H}_2\text{M}]$

$$4.0\text{e-}4 = 1.0\text{e-}3 * 5.04\text{e-}5 / [\text{H}_2\text{M}]$$

$$[\text{H}_2\text{M}] = 1.26\text{e-}4 \text{ M}$$

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

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

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

Back to the MBE

$$[\text{HM}^-] = F - [\text{H}_2\text{M}] - [\text{M}^{2-}] = 1.00\text{e-}3 - 1.26\text{e-}4 \text{ M} - 1.77\text{e-}4$$

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

Now plug this back into

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

$$= \sqrt{\frac{4.0 \times 10^{-4} \times 8.9 \times 10^{-6} \times 6.97 \times 10^{-4} + 4.0 \times 10^{-4} \times 1.00 \times 10^{-14}}{4.0 \times 10^{-4} + 6.97 \times 10^{-4}}}$$

$$= 4.76e-5 \text{ M}$$

we will find that

$$[H_2M] = 8.29e-5 \text{ M}$$

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

plug this back into the MBE

$$\text{now } [HM^-] = 7.87e-4 \text{ M}$$

$$\text{repeat 3}^{\text{rd}} \text{ time } [HM^-] = 4.86e-5$$

$$4^{\text{th}} \text{ time } [HM^-] = 4.83e-5$$

$$\text{pH} = 4.316$$

with the $5.04e-5$ which we calculated before $\text{pH} = 4.297$

$$\text{using } \text{pH} = \frac{1}{2}(\text{p}K_{a1} + \text{p}K_{a2}) = 4.224$$