In general for H_nA

$$D = [H^+]^n + K_{a1}[H^+]^{n-1} + K_{a1}K_{a2}[H^+]^{n-2} + \ldots\ldots + K_{a1}K_{a2}K_{a3}\ldots K_{an}$$

$$\alpha_{HnA} = \frac{[H^+]^n}{D}$$

$$\alpha_{Hn-1A} = \frac{K_{a1}[H^+]^{n-1}}{D}$$

$$\alpha_{Hn-jA} = \frac{K_{a1}K_{a2}\ldots K_j[H^+]^{n-j}}{D}$$

Example – Calculate the relative concentrations of the various forms of oxalic acid $H_2C_2O_4$

K_{a1} = 5.62e-2 K_{a2} = 5.42e-5

pK_{a1} = 1.250 pK_{a2} = 4.266

At pH 2.00

$D = [H^+]^2 + K_{a1}[H^+]^1 + K_{a1}K_{a2}$

$= (1.0e\text{-}2)^2 + 5.62e\text{-}2*1.0e\text{-}2 + 5.62e\text{-}2*5.42e\text{-}5 = 6.6e\text{-}4$

$\alpha_{H2A} = [H^+]^2/D = (1.0e\text{-}2)^2/6.6e\text{-}4 = 0.15$

$\alpha_{HA^-} = K_{a1}[H^+]/D = (1.0e\text{-}2*5.62e\text{-}2)/6.6e\text{-}4 = 0.85$

$\alpha_{A=} = K_{a1}\,K_{a2}/D = 5.62e\text{-}2*5.42e\text{-}5/6.6e\text{-}4 = 0.0046$

Check

$1 = \alpha_{H2A} + \alpha_{HA^-} + \alpha_{A=} = 0.15 + 0.85 + 0.0046 = 1.00$

.....

pH of amphoteric species

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

Example **0.10 M NaH_2PO_4**

Amphoteric: $H_2PO_4^- = H^+ + HPO_4^{2-}$ **&** $H_2PO_4^- + H_2O = H_3PO_4 + HO^-$

$H_3PO_4^- = H^+ + H_2PO_4^-$ K_{a1}= 7.11e-3
$H_2PO_4^- = H^+ + HPO_4^{2-}$ K_{a2}= 6.32e-8

$$[H^+] \approx \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}} = \sqrt{\frac{7.11e-3*6.32e-8*0.10 + 7.11e-3*1.00e-14}{7.11e-3 + 0.10}}$$

$[H^+] = (4.493e\text{-}11/0.107)^{1/2} = 2.05e\text{-}5$

pH = 4.69

also: pH = ½ (pK_{a1} + pK_{a2}) 9-12 8th

Example **0.10 M NaH_2PO_4**

K_{a1}= 7.11e-3 K_{a2} = 6.32e-8
pK_{a1} = 2.148 pK_{a2} = 7.199

pH = ½ (2.148 + 7.199) = 4.674

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Chapter 11

For ML_n **$\alpha_M = 1 / \{1+ \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n \}$**

Example $Ag(NH_3)_2^+$ in 0.100 M NH_3

Use Appendix I

$Ag^+ + NH_3 = Ag(NH_3)^+$ $\log \beta_1 = 3.31$ $\beta_1 = 2.04e3$
$Ag^+ + 2NH_3 = Ag(NH_3)_2^+$ $\log \beta_2 = 7.23$ $\beta_2 = 1.69e7$

$\alpha_{ag+} = 1 / \{1+ 2.04e3[0.100] + 1.69e7[0.100]^2\} = 5.91e-6$