

Chapter 9

In general for H_nA

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

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

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

$$\alpha_{H_{n-j}A} = \frac{K_{a1}K_{a2}\dots K_j[H^+]^{n-j}}{D}$$

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

$$\begin{array}{ll} K_{a1} = 5.62e-2 & K_{a2} = 5.42e-5 \\ pK_{a1} = 1.250 & pK_{a2} = 4.266 \end{array}$$

At pH 2.00

$$\begin{aligned} D &= [H^+]^2 + K_{a1}[H^+]^1 + K_{a1}K_{a2} \\ &= (1.0e-2)^2 + 5.62e-2 * 1.0e-2 + 5.62e-2 * 5.42e-5 = 6.6e-4 \end{aligned}$$

$$\alpha_{H_2A} = [H^+]^2/D = (1.0e-2)^2/6.6e-4 = 0.15$$

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

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

Check

$$1 = \alpha_{\text{H}_2\text{A}} + \alpha_{\text{HA}^-} + \alpha_{\text{A}^{2-}} = 0.15 + 0.85 + 0.0046 = 1.00$$

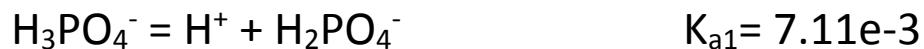
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pH of amphoteric species

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

Example **0.10 M NaH₂PO₄**

Amphoteric: $\text{H}_2\text{PO}_4^- = \text{H}^+ + \text{HPO}_4^{2-}$ & $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} = \text{H}_3\text{PO}_4 + \text{HO}^-$



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

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

$$\text{pH} = 4.69$$

$$\text{also: } \text{pH} = \frac{1}{2} (\text{pK}_{a1} + \text{pK}_{a2})$$

9-12 8th

Example **0.10 M NaH₂PO₄**

$$K_{a1} = 7.11\text{e-}3$$

$$K_{a2} = 6.32\text{e-}8$$

$$\text{pK}_{a1} = 2.148$$

$$\text{pK}_{a2} = 7.199$$

$$\text{pH} = \frac{1}{2} (2.148 + 7.199) = 4.674$$

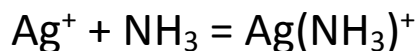
Chapter 11

For ML_n

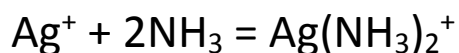
$$\alpha_M = 1 / \{1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n\}$$

Example Ag(NH₃)₂⁺ in 0.100 M NH₃

Use Appendix I



$$\log \beta_1 = 3.31 \quad \beta_1 = 2.04\text{e}3$$



$$\log \beta_2 = 7.23 \quad \beta_2 = 1.69\text{e}7$$

$$\alpha_{\text{ag}^+} = 1 / \{1 + 2.04\text{e}3[0.100] + 1.69\text{e}7[0.100]^2\} = 5.91\text{e-}6$$