

Chemistry 255  
Spring 2011  
Problem Set #4  
Answer Key

$$1. \text{pH} = \text{pK}_a + \log \frac{[\text{B}]}{[\text{BH}^+]} \quad \text{B} = \text{Tris} \quad \text{BH}^+ = \text{TrisHCl}$$

$$[\text{B}] = \frac{0.072 \text{ moles}}{2.50\text{L}} = 0.0288\text{M} \quad [\text{BH}^+] = \frac{0.038 \text{ moles}}{2.50\text{L}} = 0.0152\text{M}$$

$$\text{pK}_a = -\log(8.32 \times 10^{-9}) = 8.0799$$

$$\text{pH} = 8.0799 + \log \frac{[0.0288\text{M}]}{[0.0152\text{M}]} = 8.36$$

$$2. \text{pH} = \text{pK}_a + \log \frac{[\text{HA}^{-2}]}{[\text{H}_2\text{A}^-]} \quad 1 \text{ L total volume}$$

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

$$\text{pK}_{a2} = 7.199 \leftarrow \text{use (closest to 7.4)}$$

$$\text{pK}_{a3} = 12.15$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{HPO}_4^{-2}]}{[\text{H}_2\text{PO}_4^-]} \Rightarrow 7.40 = 7.199 + \log \frac{[2.05 \frac{\text{mol}}{\text{L}} \text{HPO}_4^{-2}](x \text{ L})}{[1.25 \frac{\text{mol}}{\text{L}} \text{H}_2\text{PO}_4^-](y \text{ L})}$$

$$1.5885 = \frac{2.05x}{1.25y}$$

$$\text{but } x + y = 1.00 \text{ L total volume} \Rightarrow y = 1.00 - x$$

$$1.5885 = \frac{2.05x}{1.25(1-x)}$$

$$2.05x = 1.9857 - 1.9857x$$

$$4.0357x = 1.9857$$

$$x = 0.4920$$

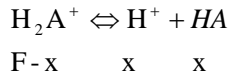
$$y = 1.00 - x = 0.50796$$

$$x = 0.492\text{L} = \text{volume HPO}_4^{-2}$$

$$y = 0.508\text{L} = \text{volume H}_2\text{PO}_4^-$$

$$3. \text{H}_2\text{A}^+ \leftrightarrow \text{H}^+ + \text{HA} \quad K_{a1} = \frac{K_w}{K_{b2}} = \frac{1.0 \times 10^{-14}}{5.49 \times 10^{-9}} = 1.82 \times 10^{-6}$$

$$\text{HA} \leftrightarrow \text{H}^+ + \text{A}^- \quad K_{a2} = \frac{K_w}{K_{b1}} = \frac{1.0 \times 10^{-14}}{7.94 \times 10^{-7}} = 1.259 \times 10^{-8}$$



Plug in to  $K_{a1}$  expression  $\frac{x^2}{8.25 \times 10^{-3} - x} = 1.82 \times 10^{-6}$

$$x^2 = 1.50 \times 10^{-8} - 1.82 \times 10^{-6} x$$

$$x^2 + 1.82 \times 10^{-6} x - 1.50 \times 10^{-8} = 0 \quad \text{solve quadratic equation}$$

$$x = \frac{-1.82 \times 10^{-6} \pm \sqrt{(1.82 \times 10^{-6})^2 - 4(-1.50 \times 10^{-8})}}{2} = 1.22 \times 10^{-4} = [\text{H}^+]$$

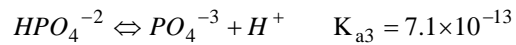
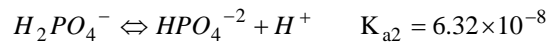
a) pH = 3.915

$$\text{b) } \alpha_{\text{H}_2\text{A}^+} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}} = \frac{(1.22 \times 10^{-4})^2}{(1.22 \times 10^{-4})^2 + 2.22 \times 10^{-10} + 2.29 \times 10^{-14}} = 0.9853$$

= 98.5%

$$\text{c) } \alpha_{\text{A}^-} = \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}} = \frac{2.29 \times 10^{-14}}{1.5106 \times 10^{-8}} = 1.517 \times 10^{-6} = 1.52 \times 10^{-4}\%$$

$$4. \text{Na}_2\text{HPO}_4 = 142 \text{ g/mol} \quad 8.24 \text{ g} \times \frac{1 \text{ mol}}{142 \text{ g}} = \frac{0.0580 \text{ mol}}{0.350 \text{ L}} = 0.1658 \text{ M}$$



$$[\text{H}^+] = \sqrt{\frac{K_{a2}K_{a3}F + K_{a2}K_w}{K_{a2} + F}} = \sqrt{\frac{(6.32 \times 10^{-8})(7.1 \times 10^{-13})(0.1658) + (6.32 \times 10^{-8})(1 \times 10^{-14})}{6.32 \times 10^{-8} + 0.1658}} = 2.206 \times 10^{-10}$$

$$\text{pH} = 9.66$$

OR

$$[\text{H}^+] = \sqrt{\frac{K_{a2}K_{a3}F + K_{a2}K_w}{K_{a2} + F}} = \sqrt{\frac{(6.34 \times 10^{-8})(4.22 \times 10^{-13})(0.1658) + (6.34 \times 10^{-8})(1 \times 10^{-14})}{6.34 \times 10^{-8} + 0.1658}} = 1.748 \times 10^{-10}$$

$$\text{pH} = 9.76$$

$$\text{b) } \text{Na}_2\text{HPO}_4 = 142 \text{ g/mol} \quad 7.29 \text{ g} \times \frac{1 \text{ mol}}{142 \text{ g}} = \frac{5.134 \times 10^{-2} \text{ mol}}{0.750 \text{ L}} = 6.845 \times 10^{-2} \text{ M}$$

$$\text{Na}_3\text{PO}_4 = 164 \text{ g/mol} \quad 5.37 \text{ g} \times \frac{1 \text{ mol}}{164 \text{ g}} = \frac{3.274 \times 10^{-2} \text{ mol}}{0.750 \text{ L}} = 4.366 \times 10^{-2} \text{ M}$$



$$\text{pH} = \text{p}K_{a3} + \log \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$

$$\text{pH} = 12.149 + \log \frac{4.366 \times 10^{-2}}{6.845 \times 10^{-2}} = 11.953 \approx 11.95$$

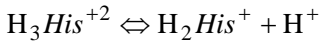
OR



$$\text{pH} = \text{p}K_{a3} + \log \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$

$$\text{pH} = 12.375 + \log \frac{4.366 \times 10^{-2}}{6.845 \times 10^{-2}} = 12.179 \approx 12.18$$

$$5. \quad 0.38 \text{ M } H_3His^{+2} \quad K_{a1} = 3 \times 10^{-2} \quad K_{a2} = 1.07 \times 10^{-6} \quad K_{a3} = 5.2 \times 10^{-10}$$



$$0.27 - x \quad x \quad x$$

$$\frac{x^2}{0.27 - x} = 3 \times 10^{-2} \Rightarrow \text{rearrange to form quadratic equation: } x^2 + 3 \times 10^{-2}x - 8.1 \times 10^{-3} = 0$$

$$x = \frac{-3 \times 10^{-2} + \sqrt{(3 \times 10^{-2})^2 + 4(8.1 \times 10^{-3})}}{2} = 7.624 \times 10^{-2} \quad pH = -\log 7.624 \times 10^{-2} = 1.118 \approx 1.1$$

$$0.27 \text{ M } H_2His^+$$

$$[H^+] \approx \sqrt{\frac{(3 \times 10^{-2})(1.07 \times 10^{-6})(0.27) + (3 \times 10^{-2})(1 \times 10^{-14})}{3 \times 10^{-2} + 0.27}} = 1.6997 \times 10^{-4}$$

$$pH = 3.8$$

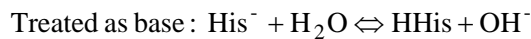
$$0.27 \text{ M } HHis$$

$$[H^+] = \sqrt{\frac{K_2 K_3 F + K_2 K_w}{K_2 + F}} = \sqrt{\frac{(1.07 \times 10^{-6})(5.2 \times 10^{-10})(0.27) + (1.07 \times 10^{-6})(1 \times 10^{-14})}{(1.07 \times 10^{-6}) + 0.27}} = 2.359 \times 10^{-8}$$

$$pH = 7.63$$

$$0.27 \text{ M } His^-$$

$$K_{b1} = \frac{K_w}{K_{a3}} = \frac{1 \times 10^{-14}}{5.2 \times 10^{-10}} = 1.92 \times 10^{-5}$$



$$0.27 - x \quad x \quad x$$

$$K_{b1} = \frac{[HHis][OH^-]}{[His^-]} = \frac{x^2}{0.27 - x} = 1.92 \times 10^{-5} \quad \text{arrange as quadratic equation}$$

$$x^2 + 1.92 \times 10^{-5}x - 5.19 \times 10^{-6} = 0 \Rightarrow x = \frac{-1.92 \times 10^{-5} \pm \sqrt{(1.92 \times 10^{-5})^2 - 4(-5.19 \times 10^{-6})}}{2}$$

$$x = 2.269 \times 10^{-3} = [OH^-]$$

$$pOH = 2.644$$

$$pH = 11.36$$

$$6. K_{a1} = 1.07 \times 10^{-3} \quad pK_{a1} = 2.971$$

$$K_{a2} = 1.82 \times 10^{-14} \quad pK_{a2} = 13.740$$

a) Principal Species :  $H_2S$  fully protonated

pH is less than  $pK_{a1}$

$$pK_{a1} = 2.971 \quad pH = 2.50$$

$$pH = pK_{a1} + \log \frac{[HS^-]}{[H_2S]}$$

$$2.50 = 2.971 + \log \frac{[HS^-]}{[H_2S]}$$

$$\frac{[HS^-]}{[H_2S]} = 0.338$$

$$[HS^-] = 0.338[H_2S]$$

b) Principal Species :  $HS^-$  ( $CO_2^-$ ) intermediate

pH between  $pK_{a1}$  and  $pK_{a2}$

$$pK_{a1} = 2.971 \quad pH = 7.40$$

$$pH = pK_{a1} + \log \frac{[HS^-]}{[H_2S]}$$

$$7.40 = 2.971 + \log \frac{[HS^-]}{[H_2S]}$$

$$\frac{[HS^-]}{[H_2S]} = 26853$$

$$[HS^-] = 26853[H_2S]$$

$$pK_{a2} = 13.740 \quad pH = 7.40$$

$$pH = pK_{a2} + \log \frac{[S^{2-}]}{[HS^-]}$$

$$7.40 = 13.740 + \log \frac{[S^{2-}]}{[HS^-]}$$

$$\frac{[S^{2-}]}{[HS^-]} = 4.57 \times 10^{-7}$$

$$[S^{2-}] = 4.57 \times 10^{-7} [HS^-]$$

7.

$$\alpha_{\text{H}_2\text{A}^+} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}} = \frac{(1.00 \times 10^{-7})^2}{(1.00 \times 10^{-7})^2 + (1.00 \times 10^{-7})(1.00 \times 10^{-8}) + (1.00 \times 10^{-8})(1.00 \times 10^{-10})} = 0.91$$

= 91%