Chemistry 255
Spring 2011
Problem Set #4
Answer Key

1. $pH = pK_a + \log\frac{[B]}{[BH^+]}$ B = Tris $BH^+$ = TrisHCl

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

$pK_a = -\log(8.32\times10^{-9}) = 8.0799$

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

2. $pH = pK_a + \log\frac{[HA^{-2}]}{[H_2A^-]}$ 1 L total volume

$pK_{a1} = 2.148$

$pK_{a2} = 7.199 \Leftarrow$ use (closest to 7.4)

$pK_{a3} = 12.15$

$pH = pK_a + \log\frac{[HPO_4{}^{-2}]}{[H_2PO_4{}^-]} \Rightarrow 7.40 = 7.199 + \log\frac{[2.05\ \frac{\text{mol}}{\text{L}}\ HPO_4{}^{-2}](x\ \text{L})}{[1.25\ \frac{\text{mol}}{\text{L}}\ H_2PO_4{}^-](y\ \text{L})}$

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

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

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

$2.05x = 1.9857 - 1.9857x$

$4.0357x = 1.9857$

$x = 0.4920$

$y = 1.00 - x = 0.50796$

$x = 0.492\text{L} = \text{volume}\ HPO_4{}^{-2}$

$y = 0.508\text{L} = \text{volume}\ H_2PO_4{}^-$

3. $H_2A^+ \Leftrightarrow H^+ + HA$ $\quad K_{a1} = \dfrac{K_w}{K_{b2}} = \dfrac{1.0x10^{-14}}{5.49x10^{-9}} = 1.82\times10^{-6}$

$HA \Leftrightarrow H^+ + A^-$ $\quad K_{a2} = \dfrac{K_w}{K_{b1}} = \dfrac{1.0x10^{-14}}{7.94x10^{-7}} = 1.259\times10^{-8}$

$H_2A^+ \Leftrightarrow H^+ + HA$

F - x $\quad$ x $\quad$ x

Plug in to $K_{a1}$ expression $\quad \dfrac{x^2}{8.25\times10^{-3} - x} = 1.82\times10^{-6}$

$x^2 = 1.50\times10^{-8} - 1.82\times10^{-6}x$

$x^2 + 1.82\times10^{-6}x - 1.50\times10^{-8} = 0$ $\quad$ solve quadratic equation

$$x = \frac{-1.82\times10^{-6} \pm \sqrt{(1.82\times10^{-6})^2 - 4(-1.50\times10^{-8})}}{2} = 1.22\times10^{-4} = [H^+]$$

*a*) pH = 3.915

b) $\alpha_{H_2A^+} = \dfrac{[H^+]^2}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}} = \dfrac{(1.22\times10^{-4})^2}{(1.22\times10^{-4})^2 + 2.22\times10^{-10} + 2.29\times10^{-14}} = 0.9853$

$= 98.5\%$

c) $\alpha_{A^-} = \dfrac{K_{a1}K_{a2}}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}} = \dfrac{2.29\times10^{-14}}{1.5106\times10^{-8}} = 1.517x10^{-6} = 1.52x10^{-4}\%$

4. $Na_2HPO_4 = 142\ \text{g/mol} \quad 8.24\ \text{g} \times \frac{1\ \text{mol}}{142\ \text{g}} = \frac{0.0580\ \text{mol}}{0.350\ \text{L}} = 0.1658M$

$H_2PO_4^- \Leftrightarrow HPO_4^{-2} + H^+ \qquad K_{a2} = 6.32\times10^{-8}$

$HPO_4^{-2} \Leftrightarrow PO_4^{-3} + H^+ \qquad K_{a3} = 7.1\times10^{-13}$

$$[H^+] = \sqrt{\frac{K_{a2}K_{a3}F + K_{a2}K_w}{K_{a2} + F}} = \sqrt{\frac{(6.32\times10^{-8})(7.1\times10^{-13})(0.1658) + (6.32\times10^{-8})(1\times10^{-14})}{6.32\times10^{-8} + 0.1658}} = 2.206\times10^{-10}$$

$pH = 9.66$

*OR*

$$[H^+] = \sqrt{\frac{K_{a2}K_{a3}F + K_{a2}K_w}{K_{a2} + F}} = \sqrt{\frac{(6.34\times10^{-8})(4.22\times10^{-13})(0.1658) + (6.34\times10^{-8})(1\times10^{-14})}{6.34\times10^{-8} + 0.1658}} = 1.748\times10^{-10}$$

$pH = 9.76$

b) $Na_2HPO_4 = 142\ \text{g/mol} \qquad 7.29\ \text{g} \times \frac{1\ \text{mol}}{142\ \text{g}} = \frac{5.134\times10^{-2}\ \text{mol}}{0.750\ \text{L}} = 6.845\times10^{-2}M$

$Na_3PO_4 = 164\ \text{g/mol} \qquad 5.37\ \text{g} \times \frac{1\ \text{mol}}{164\ \text{g}} = \frac{3.274\times10^{-2}\ mol}{0.750\ \text{L}} = 4.366\times10^{-2}M$

$HPO_4^{-2} \Leftrightarrow PO_4^{-3} + H^+ \qquad K_{a3} = 7.1\times10^{-13} \qquad pK_{a3} = 12.149$

$$pH = pKa_3 + \log\frac{[PO_4^{-3}]}{[HPO_4^{-2}]}$$

$$pH = 12.149 + \log\frac{4.366\times10^{-2}}{6.845\times10^{-2}} = 11.953 \approx 11.95$$

OR

$HPO_4^{-2} \Leftrightarrow PO_4^{-3} + H^+ \qquad K_{a3} = 4.22\times10^{-13} \qquad pK_{a3} = 12.375$

$$pH = pKa_3 + \log\frac{[PO_4^{-3}]}{[HPO_4^{-2}]}$$

$$pH = 12.375 + \log\frac{4.366\times10^{-2}}{6.845\times10^{-2}} = 12.179 \approx 12.18$$

5. 0.38 M $H_3His^{+2}$ $K_{a1} = 3\times10^{-2}$ $K_{a2} = 1.07\times10^{-6}$ $K_{a3} = 5.2\times10^{-10}$

$H_3His^{+2} \Leftrightarrow H_2His^{+} + H^{+}$

$0.27 - x$ x x

$\frac{x^2}{0.27 - x} = 3\times10^{-2} \Rightarrow$ rearrage to form quadratic equation : $x^2 + 3\times10^{-2}x - 8.1\times10^{-3} = 0$

$x = \frac{-3\times10^{-2} + \sqrt{(3\times10^{-2})^2 + 4(8.1\times10^{-3})}}{2} = 7.624\times10^{-2}$ $pH = -\log 7.624\times10^{-2} = 1.118 \approx 1.1$

0.27 M $H_2His^{+}$

$[H^+] \approx \sqrt{\frac{(3\times10^{-2})(1.07\times10^{-6})(0.27) + (3\times10^{-2})(1\times10^{-14})}{3\times10^{-2} + 0.27}} = 1.6997\times10^{-4}$

$pH = 3.8$

0.27 M HHis

$[H^+] = \sqrt{\frac{K_2K_3F + K_2K_w}{K_2 + F}} = \sqrt{\frac{(1.07\times10^{-6})(5.2\times10^{-10})(0.27) + (1.07\times10^{-6})(1\times10^{-14})}{(1.07\times10^{-6}) + 0.27}} = 2.359\times10^{-8}$

$pH = 7.63$

0.27 M $His^-$

$K_{b1} = \frac{K_w}{K_{a3}} = \frac{1\times10^{-14}}{5.2\times10^{-10}} = 1.92\times10^{-5}$

Treated as base : $His^- + H_2O \Leftrightarrow HHis + OH^-$

$0.27 - x$ x x

$K_{b1} = \frac{[HHis][OH^-]}{[His^-]} = \frac{x^2}{0.27 - x} = 1.92\times10^{-5}$ arrange as quadratic equation

$x^2 + 1.92\times10^{-5}x - 5.19\times10^{-6} = 0 \Rightarrow x = \frac{-1.92\times10^{-5} \pm \sqrt{(1.92\times10^{-5})^2 - 4(-5.19\times10^{-6})}}{2}$

$x = 2.269\times10^{-3} = [OH^-]$

$pOH = 2.644$

$pH = 11.36$

6. $K_{a1} = 1.07 \times 10^{-3}$ $pKa_1 = 2.971$

$K_{a2} = 1.82 \times 10^{-14}$ $pKa_2 = 13.740$

a) Principal Species : $H_2S$ fully protonated

pH is less than $pK_{a1}$

$pKa_1 = 2.971$ $pH = 2.50$

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

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

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

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

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

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

$pKa_1 = 2.971$ $pH = 7.40$

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

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

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

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

$pKa_2 = 13.740$ $pH = 7.40$

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

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

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

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

7.

$$\alpha_{H_2A^+} = \frac{[H^+]^2}{[H^+]^2 + [H^+]K_{a1} + K_{a1}K_{a2}} = \frac{(1.00\times10^{-7})^2}{(1.00\times10^{-7})^2 + (1.00\times10^{-7})(1.00\times10^{-8}) + (1.00\times10^{-8})(1.00\times10^{-10})} = 0.91$$

$= 91\%$