

Extra Credit Problem 1: Calculation of the distribution of different forms of phosphate in a 0.01 M solution at pH 7.0. Use the values 2.2, 7.2 and 12.4 for pK₁, pK₂ and pK₃ respectively.

You have the following four equations in four unknowns

$$1. \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 10^{\text{pH}-\text{pK}} = 10^{7.0-2.2} = 10^{4.8} = 6.31 \times 10^4$$

$$[\text{H}_2\text{PO}_4^-] = [\text{H}_3\text{PO}_4] \times 6.31 \times 10^4$$

$$2. \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 10^{\text{pH}-\text{pK}} = 10^{7.0-7.2} = 10^{-0.2} = 0.631$$

$$[\text{HPO}_4^{2-}] = [\text{H}_2\text{PO}_4^-] \times 0.631$$

$$3. \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 10^{\text{pH}-\text{pK}} = 10^{7.0-12.4} = 10^{-5.4} = 3.98 \times 10^{-6}$$

$$[\text{PO}_4^{3-}] = [\text{HPO}_4^{2-}] \times 3.98 \times 10^{-6}$$

$$4. [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] = 0.01 \text{M}$$

Substitute 1 for $[\text{H}_2\text{PO}_4^-]$ in 2:

$$2. [\text{HPO}_4^{2-}] = [\text{H}_3\text{PO}_4] \times 6.31 \times 10^4 \times 0.631$$

Substitute 2 for $[\text{HPO}_4^{2-}]$ in 3:

$$3. [\text{PO}_4^{3-}] = [\text{H}_3\text{PO}_4] \times 6.31 \times 10^4 \times 0.631 \times 3.98 \times 10^{-6}$$

Substitute 1, 2, and 3 into 4 to get 4 as a function of $[\text{H}_3\text{PO}_4]$

$$4. [\text{H}_3\text{PO}_4]$$

$$+ [\text{H}_3\text{PO}_4] \times 6.31 \times 10^4$$

$$+ [\text{H}_3\text{PO}_4] \times 6.31 \times 10^4 \times 0.631$$

$$+ [\text{H}_3\text{PO}_4] \times 6.31 \times 10^4 \times 0.631 \times 3.98 \times 10^{-6} = 0.01 \text{M}$$

Factor:

$$[\text{H}_3\text{PO}_4](1 + 6.31 \times 10^4 + 6.31 \times 10^4 \times 0.631 + 6.31 \times 10^4 \times 0.631 \times 3.98 \times 10^{-6}) = 0.01 \text{M}$$

$$[\text{H}_3\text{PO}_4](1.02917 \times 10^5) = 0.01 \text{M}$$

$$[\text{H}_3\text{PO}_4] = \frac{0.01 \text{M}}{1.02917 \times 10^5} = 9.71654 \times 10^{-8} \text{M}$$

Then plug this value into equations 1, 2, and 3:

$$[\text{H}_2\text{PO}_4^-] = 9.71654 \times 10^{-8} \text{M} \times 6.31 \times 10^4 = 6.1311 \times 10^{-3} = 0.0061311 \text{M}$$

$$[\text{HPO}_4^{2-}] = 9.71654 \times 10^{-8} \text{M} \times 6.31 \times 10^4 \times 0.631 = 3.86875 \times 10^{-3} = 0.00386875 \text{M}$$

$$[\text{PO}_4^{3-}] = 9.71654 \times 10^{-8} \text{M} \times 6.31 \times 10^4 \times 0.631 \times 3.98 \times 10^{-6} = 1.53976 \times 10^{-8} \text{M}$$

Check the answers by plugging into equation 4:

$$9.71654 \times 10^{-8} + 0.0061311 + 0.00386875 + 1.53976 \times 10^{-8} = 9.999996 \times 10^{-3} \text{ or } 0.01$$

I carried this out to way too many significant figures to make a point. Actually one should round off for the two major species:

$$[\text{H}_2\text{PO}_4^-] = 0.0061311 \text{ and } [\text{HPO}_4^{2-}] = 0.00386875 \text{ M}$$

and recognize that the minor species are well below significant concentrations, yet there is some of each species present.