11.9: Calculation of the Composition of a Weak Polyprotic Acid Using Mathcad

Polyprotic Acids - Calculating the composition of 0.1M H_3AsO_4

Excluding water there are six species in this solution of arsenic acid. Therefore six constraints are required to calculate the composition of the solution. Four of them are the following equilibria, and the other two are the charge and mass balance equations given below.

Equilibria:

$$\mathrm{H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-}$$

$$\mathrm{H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-}}$$

$$\mathrm{HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-}}$$

$$\mathrm{H_2O \rightleftharpoons H^+ + OH^-}$$

Charge balance:

$$[\mathrm{H^+}] = [\mathrm{H_2AsO_4^-}] + 2[\mathrm{HAsO_4^{2-}}] + 3[\mathrm{AsO_4^{3-}}] + [\mathrm{OH^-}]$$

Mass balance:

$$H_3AsO_4 + H_2AsO_4^{-} + HAsO_4^{2-} + AsO_4^{3-} = 0.1$$

Relevant equilibrium constants:

$$Ka1 := 4.5 \times 10^{-4} \ Ka2 := 5.6 \times 10^{-8} \ Ka3 := 3.0 \times 10^{-13} \ Kw := 10^{-14}$$

Mathcad's live symbolic solver is used to calculate the concentrations of the species in solution by creating two 6x1 vectors. In one vector the six constraints are entered, and in the other the symbols for the species being calculated. The results of the calculation are given below.

$$\begin{pmatrix} \frac{H \cdot H_2AsO_4}{H_3AsO_4} = Ka1 \\ \frac{H \cdot HAsO_4}{H_2AsO_4} = Ka2 \\ \frac{H \cdot AsO_4}{HAsO_4} = Ka3 \\ H \cdot OH = Kw \\ H = H_2AsO_4 + 2 \cdot HAsO_4 + 3 \cdot AsO_4 + OH \\ H_3AsO_4 + H_2AsO_4 + HAsO_4 + AsO_4 = 0.1 \end{pmatrix} \begin{array}{l} solve, \begin{pmatrix} H \\ H_3AsO_4 \\ H_2AsO_4 \\ HAsO_4 \\ AsO_4 \\ OH \end{pmatrix} \\ \\ float,3 \end{array}$$

$$\rightarrow \begin{pmatrix} -6.94 \cdot 10^{-3} & .107 & -6.94 \cdot 10^{-3} & -2.42 \cdot 10^{-18} & -1.44 \cdot 10^{-12} & \\ -1.12 \cdot 10^{-7} & -4.98 \cdot 10^{-5} & 0.200 & -.100 & 2.68 \cdot 10^{-7} & -8.93 \cdot 10^{-8} \\ -4.68 \cdot 10^{-13} & 2.42 \cdot 10^{-15} & -2.33 \cdot 10^{-6} & .279 & -.179 & -2.14 \cdot 10^{-2} \\ -3.21 \cdot 10^{-14} & -4.88 \cdot 10^{-}19 & 6.85 \cdot 10^{-9} & -1.20 \cdot 10^{-2} & .112 & -.312 \\ 6.49 \cdot 10^{-3} & 9.35 \cdot 10^{-}2 & 6.49 \cdot 10^{-3} & 5.60 \cdot 10^{-8} & 2.59 \cdot 10^{-18} & 1.54 \cdot 10^{-12} \end{pmatrix}$$

The last row contains the physically meaningful solution to the fifth order polynomial that is solved. The pH of this solution is calculated below.

$$pH := -\log(6.49 \times 10^{-3}) \ pH = 2.188$$