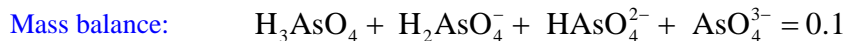
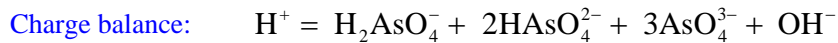
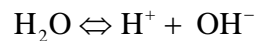
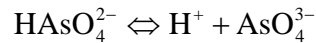
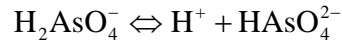
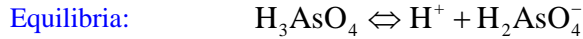


Polyprotic Acids - Calculating the composition of 0.1M H₃AsO₄

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.



Relevant equilibrium constants:

$$K_{a1} := 4.5 \cdot 10^{-4}$$

$$K_{a2} := 5.6 \cdot 10^{-8}$$

$$K_{a3} := 3.0 \cdot 10^{-13}$$

$$K_w := 10^{-14}$$

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.

$$\left(\begin{array}{l} \frac{\text{H} \cdot \text{H}_2\text{AsO}_4}{\text{H}_3\text{AsO}_4} = K_{a1} \\ \frac{\text{H} \cdot \text{HAsO}_4}{\text{H}_2\text{AsO}_4} = K_{a2} \\ \frac{\text{H} \cdot \text{AsO}_4}{\text{HAsO}_4} = K_{a3} \\ \text{H} \cdot \text{OH} = K_w \\ \text{H} = \text{H}_2\text{AsO}_4 + 2 \cdot \text{HAsO}_4 + 3 \cdot \text{AsO}_4 + \text{OH} \\ \text{H}_3\text{AsO}_4 + \text{H}_2\text{AsO}_4 + \text{HAsO}_4 + \text{AsO}_4 = .1 \end{array} \right) \left. \begin{array}{l} \text{solve,} \\ \text{float, 3} \end{array} \right\} \left(\begin{array}{l} \text{H} \\ \text{H}_3\text{AsO}_4 \\ \text{H}_2\text{AsO}_4 \\ \text{HAsO}_4 \\ \text{AsO}_4 \\ \text{OH} \end{array} \right) \rightarrow \left(\begin{array}{cccccc} -6.94 \cdot 10^{-3} & .107 & -6.94 \cdot 10^{-3} & 5.60 \cdot 10^{-8} & -2.42 \cdot 10^{-18} & -1.44 \cdot 10^{-12} \\ -1.12 \cdot 10^{-7} & -4.98 \cdot 10^{-5} & .200 & -.100 & 2.68 \cdot 10^{-7} & -8.93 \cdot 10^{-8} \\ -4.68 \cdot 10^{-13} & 2.42 \cdot 10^{-15} & -2.33 \cdot 10^{-6} & .279 & -.179 & -2.14 \cdot 10^{-2} \\ -3.21 \cdot 10^{-14} & -4.88 \cdot 10^{-19} & 6.85 \cdot 10^{-9} & -1.20 \cdot 10^{-2} & .112 & -.312 \\ 6.49 \cdot 10^{-3} & 9.35 \cdot 10^{-2} & 6.49 \cdot 10^{-3} & 5.60 \cdot 10^{-8} & 2.59 \cdot 10^{-18} & 1.54 \cdot 10^{-12} \end{array} \right)$$

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

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