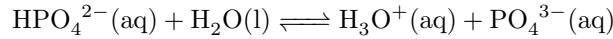
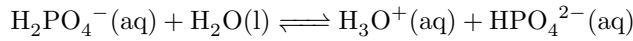
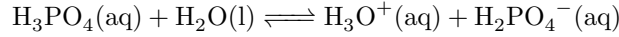


Supplementary Information

Derivation 1. *The expression of the fractional composition of various counterions as a function of hydronium ion concentration.*

Proof. First, we consider the acidity dissociation K_a values of each successive deprotonation of H_3PO_4 .



$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \quad K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \quad K_{a3} = \frac{[\text{H}_3\text{O}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$

Thereafter, we consider that the initial concentration of phosphoric acid in aqueous solution P , can be expressed as the sum of the concentration of phosphoric acid in all its forms.

$$\begin{aligned} \text{initial concentration } P &= [\text{H}_3\text{PO}_4]_{\text{as prepared}} \\ &= [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] \end{aligned}$$

We then manipulate the K_a expressions such that all species concentrations can be expressed in terms of $[\text{H}_3\text{PO}_4]$ and $[\text{H}_3\text{O}^+]$, along with the three acidity constants.

$$\begin{aligned} [\text{H}_2\text{PO}_4^-] &= \frac{K_{a1}[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]} \\ [\text{HPO}_4^{2-}] &= \frac{K_{a1}K_{a2}[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]^2} \\ [\text{PO}_4^{3-}] &= \frac{K_{a1}K_{a2}K_{a3}[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]^3} \end{aligned}$$

The above results are then substituted into the expression for P .

$$\begin{aligned} P &= [\text{H}_3\text{PO}_4] + \frac{K_{a1}[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]} + \frac{K_{a1}K_{a2}[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]^2} + \frac{K_{a1}K_{a2}K_{a3}[\text{H}_3\text{PO}_4]}{[\text{H}_3\text{O}^+]^3} \\ &= \left\{ 1 + \frac{K_{a1}}{[\text{H}_3\text{O}^+]} + \frac{K_{a1}K_{a2}}{[\text{H}_3\text{O}^+]^2} + \frac{K_{a1}K_{a2}K_{a3}}{[\text{H}_3\text{O}^+]^3} \right\} [\text{H}_3\text{PO}_4] \\ &= \frac{1}{[\text{H}_3\text{O}^+]^3} \{ [\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 K_{a1} + [\text{H}_3\text{O}^+] K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3} \} [\text{H}_3\text{PO}_4] \end{aligned}$$

Factoring out the $\frac{1}{[\text{H}_3\text{O}^+]^3}$ term will make manipulation easier, as we will see in the next steps. Now we express each species fraction as a dissociation degree, as a function of $[\text{H}_3\text{O}^+]$.

$$\begin{aligned}
\alpha_{\text{H}_3\text{PO}_4} &= \frac{[\text{H}_3\text{PO}_4]}{P} \\
&= \frac{[\text{H}_3\text{PO}_4]}{\frac{1}{[\text{H}_3\text{O}^+]^3} \{ [\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 K_{a1} + [\text{H}_3\text{O}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3} \} [\text{H}_3\text{PO}_4]} \\
&= \frac{[\text{H}_3\text{O}^+]^3}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 K_{a1} + [\text{H}_3\text{O}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3}} \quad (1)
\end{aligned}$$

$$\begin{aligned}
\alpha_{\text{H}_2\text{PO}_4^-} &= \frac{[\text{H}_2\text{PO}_4^-]}{P} \\
&= \frac{K_{a1} [\text{H}_3\text{PO}_4]}{P [\text{H}_3\text{O}^+]} \\
&= \frac{K_{a1} [\text{H}_3\text{PO}_4]}{\frac{1}{[\text{H}_3\text{O}^+]^3} \{ [\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 K_{a1} + [\text{H}_3\text{O}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3} \} [\text{H}_3\text{PO}_4] [\text{H}_3\text{O}^+]} \\
&= \frac{K_{a1} [\text{H}_3\text{O}^+]^2}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 K_{a1} + [\text{H}_3\text{O}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3}} \quad (2)
\end{aligned}$$

$$\begin{aligned}
\alpha_{\text{HPO}_4^{2-}} &= \frac{[\text{HPO}_4^{2-}]}{P} \\
&= \frac{K_{a1} K_{a2} [\text{H}_3\text{PO}_4]}{P [\text{H}_3\text{O}^+]^2} \\
&= \frac{K_{a1} K_{a2} [\text{H}_3\text{PO}_4]}{\frac{1}{[\text{H}_3\text{O}^+]^3} \{ [\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 K_{a1} + [\text{H}_3\text{O}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3} \} [\text{H}_3\text{PO}_4] [\text{H}_3\text{O}^+]^2} \\
&= \frac{K_{a1} K_{a2} [\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 K_{a1} + [\text{H}_3\text{O}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3}} \quad (3)
\end{aligned}$$

$$\begin{aligned}
\alpha_{\text{PO}_4^{3-}} &= \frac{[\text{PO}_4^{3-}]}{P} \\
&= \frac{K_{a1} K_{a2} K_{a3} [\text{H}_3\text{PO}_4]}{P [\text{H}_3\text{O}^+]^3} \\
&= \frac{K_{a1} K_{a2} K_{a3} [\text{H}_3\text{PO}_4]}{\frac{1}{[\text{H}_3\text{O}^+]^3} \{ [\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 K_{a1} + [\text{H}_3\text{O}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3} \} [\text{H}_3\text{PO}_4] [\text{H}_3\text{O}^+]^3} \\
&= \frac{K_{a1} K_{a2} K_{a3}}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 K_{a1} + [\text{H}_3\text{O}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3}} \quad (4)
\end{aligned}$$

□