Supplementary Information

Derivation 1. *The expression of the fractional composition of various phosphate counteranions at different hydrolysis states as a function of hydronium ion concentration.*

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

$$\begin{aligned}
H_3PO_4(aq) + H_2O(l) &\rightleftharpoons H_3O^+(aq) + H_2PO_4{}^-(aq)\\
H_2PO_4{}^-(aq) + H_2O(l) &\rightleftharpoons H_3O^+(aq) + HPO_4{}^{2-}(aq)\\
HPO_4{}^{2-}(aq) + H_2O(l) &\rightleftharpoons H_3O^+(aq) + PO_4{}^{3-}(aq)
\end{aligned}$$

$$K_{a1} = \frac{[H_3O^+][H_2PO_4{}^-]}{[H_3PO_4]} \qquad K_{a2} = \frac{[H_3O^+][HPO_4{}^{2-}]}{[H_2PO_4{}^-]} \qquad K_{a3} = \frac{[H_3O^+][PO_4{}^{3-}]}{[HPO_4{}^{2-}]}$$

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.

$$\begin{aligned}
\text{initial concentration } P &= [H_3PO_4]_{\text{as prepared}}\\
&= [H_3PO_4] + [H_2PO_4{}^-] + [HPO_4{}^{2-}] + [PO_4{}^{3-}]
\end{aligned}$$

We then manipulate the K_a expressions such the concentrations of all species present can be expressed in terms of $[H_3PO_4]$ and $[H_3O^+]$, along with the three acidity constants.

$$\begin{aligned}
[H_2PO_4{}^-] &= \frac{K_{a1}[H_3PO_4]}{[H_3O^+]}\\
[HPO_4{}^{2-}] &= \frac{K_{a1}K_{a2}[H_3PO_4]}{[H_3O^+]}\\
[PO_4{}^{3-}] &= \frac{K_{a1}K_{a2}K_{a3}[H_3PO_4]}{[H_3O^+]}
\end{aligned}$$

The above results are then substituted into the expression for P, followed by factoring out the common $[H_3PO_4]$ term.

$$\begin{aligned}
P &= [H_3PO_4] + \frac{K_{a1}[H_3PO_4]}{[H_3O^+]} + \frac{K_{a1}K_{a2}[H_3PO_4]}{[H_3O^+]} + \frac{K_{a1}K_{a2}K_{a3}[H_3PO_4]}{[H_3O^+]}\\
&= \left\{1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}K_{a2}}{[H_3O^+]^2} + \frac{K_{a1}K_{a2}K_{a3}}{[H_3O^+]^3}\right\}[H_3PO_4]\\
&= \frac{1}{[H_3O^+]^3}\{[H_3O^+]^3 + [H_3O^+]^2K_{a1} + [H_3O^+]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}\}[H_3PO_4]
\end{aligned}$$

Factoring out the $\frac{1}{[H_3O^+]^3}$ 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 $[H_3O^+]$.

$$
\begin{aligned}
\alpha_{H_3PO_4} &= \frac{[H_3PO_4]}{P} \\
&= \frac{[H_3PO_4]}{\frac{1}{[H_3O^+]^3}\{[H_3O^+]^3 + [H_3O^+]^2K_{a1} + [H_3O^+]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}\}[H_3PO_4]} \\
&= \frac{[H_3O^+]^3}{[H_3O^+]^3 + [H_3O^+]^2K_{a1} + [H_3O^+]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}} \qquad (1)
\end{aligned}
$$

$$
\begin{aligned}
\alpha_{H_2PO_4{}^-} &= \frac{[H_2PO_4{}^-]}{P} \\
&= \frac{K_{a1}[H_3PO_4]}{P[H_3O^+]} \\
&= \frac{K_{a1}[H_3PO_4]}{\frac{1}{[H_3O^+]^3}\{[H_3O^+]^3 + [H_3O^+]^2K_{a1} + [H_3O^+]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}\}[H_3PO_4][H_3O^+]} \\
&= \frac{K_{a1}[H_3O^+]^2}{[H_3O^+]^3 + [H_3O^+]^2K_{a1} + [H_3O^+]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}} \qquad (2)
\end{aligned}
$$

$$
\begin{aligned}
\alpha_{HPO_4{}^{2-}} &= \frac{[HPO_4{}^{2-}]}{P} \\
&= \frac{K_{a1}K_{a2}[H_3PO_4]}{P[H_3O^+]^2} \\
&= \frac{K_{a1}K_{a2}[H_3PO_4]}{\frac{1}{[H_3O^+]^3}\{[H_3O^+]^3 + [H_3O^+]^2K_{a1} + [H_3O^+]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}\}[H_3PO_4][H_3O^+]^2} \\
&= \frac{K_{a1}K_{a2}[H_3O^+]}{[H_3O^+]^3 + [H_3O^+]^2K_{a1} + [H_3O^+]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}} \qquad (3)
\end{aligned}
$$

$$
\begin{aligned}
\alpha_{PO_4{}^{3-}} &= \frac{[PO_4{}^{3-}]}{P} \\
&= \frac{K_{a1}K_{a2}K_{a3}[H_3PO_4]}{P[H_3O^+]^3} \\
&= \frac{K_{a1}K_{a2}K_{a3}[H_3PO_4]}{\frac{1}{[H_3O^+]^3}\{[H_3O^+]^3 + [H_3O^+]^2K_{a1} + [H_3O^+]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}\}[H_3PO_4][H_3O^+]^3} \\
&= \frac{K_{a1}K_{a2}K_{a3}}{[H_3O^+]^3 + [H_3O^+]^2K_{a1} + [H_3O^+]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}} \qquad (4)
\end{aligned}
$$

The above fractions are then plotted against pH in Fig. 3.

□