## 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  $\mathrm{H_3PO_4}$ .

$$\begin{split} H_{3}PO_{4}(aq) + H_{2}O(l) & \Longrightarrow H_{3}O^{+}(aq) + H_{2}PO_{4}^{-}(aq) \\ H_{2}PO_{4}^{-}(aq) + H_{2}O(l) & \Longrightarrow H_{3}O^{+}(aq) + HPO_{4}^{2-}(aq) \\ HPO_{4}^{2-}(aq) + H_{2}O(l) & \Longrightarrow H_{3}O^{+}(aq) + PO_{4}^{3-}(aq) \\ K_{a1} &= \frac{[H_{3}O^{+}][H_{2}PO_{4}^{-}]}{[H_{3}PO_{4}]} \qquad K_{a2} &= \frac{[H_{3}O^{+}][HPO_{4}^{2-}]}{[H_{2}PO_{4}^{-}]} \qquad K_{a3} &= \frac{[H_{3}O^{+}][PO_{4}^{3-}]}{[HPO_{4}^{2-}]} \end{split}$$

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.

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

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

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

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

$$P = [H_{3}PO_{4}] + \frac{K_{a1}[H_{3}PO_{4}]}{[H_{3}O^{+}]} + \frac{K_{a1}K_{a2}[H_{3}PO_{4}]}{[H_{3}O^{+}]} + \frac{K_{a1}K_{a2}K_{a3}[H_{3}PO_{4}]}{[H_{3}O^{+}]}$$

$$= \left\{1 + \frac{K_{a1}}{[H_{3}O^{+}]} + \frac{K_{a1}K_{a2}}{[H_{3}O^{+}]^{2}} + \frac{K_{a1}K_{a2}K_{a3}}{[H_{3}O^{+}]^{3}}\right\} [H_{3}PO_{4}]$$

$$= \frac{1}{[H_{3}O^{+}]^{3}} \{[H_{3}O^{+}]^{3} + [H_{3}O^{+}]^{2}K_{a1} + [H_{3}O^{+}]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}\} [H_{3}PO_{4}]$$

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  $[H_3O^+]$ .

$$\alpha_{\mathrm{H_{3}PO_{4}}} = \frac{[\mathrm{H_{3}PO_{4}}]}{P}$$

$$= \frac{[\mathrm{H_{3}PO_{4}}]}{\frac{1}{[\mathrm{H_{3}O^{+}}]^{3}} \{ [\mathrm{H_{3}O^{+}}]^{3} + [\mathrm{H_{3}O^{+}}]^{2} K_{a1} + [\mathrm{H_{3}O^{+}}] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3} \} [\mathrm{H_{3}PO_{4}}]}$$

$$= \frac{[\mathrm{H_{3}O^{+}}]^{3}}{[\mathrm{H_{3}O^{+}}]^{3} + [\mathrm{H_{3}O^{+}}]^{2} K_{a1} + [\mathrm{H_{3}O^{+}}] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3}}$$
(1)

$$\alpha_{\text{H}_2\text{PO}_4^-} = \frac{[\text{H}_2\text{PO}_4^-]}{P}$$

$$= \frac{K_{a1}[\text{H}_3\text{PO}_4]}{P[\text{H}_3\text{O}^+]}$$

$$= \frac{K_{a1}[\text{H}_3\text{PO}_4]}{\frac{1}{[\text{H}_3\text{O}^+]^3} \{[\text{H}_3\text{O}^+]^2 K_{a1} + [\text{H}_3\text{O}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3} \}[\text{H}_3\text{PO}_4][\text{H}_3\text{O}^+]}$$

$$= \frac{K_{a1}[\text{H}_3\text{O}^+]^2}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2 K_{a1} + [\text{H}_3\text{O}^+] K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3}}$$
(2)

$$\alpha_{\text{HPO}_4^{2-}} = \frac{[\text{HPO}_4^{2-}]}{P}$$

$$= \frac{K_{a1}K_{a2}[\text{H}_3\text{PO}_4]}{P[\text{H}_3\text{O}^+]^2}$$

$$= \frac{K_{a1}K_{a2}[\text{H}_3\text{PO}_4]}{\frac{1}{[\text{H}_3\text{O}^+]^3}\{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2K_{a1} + [\text{H}_3\text{O}^+]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}\}[\text{H}_3\text{PO}_4][\text{H}_3\text{O}^+]^2}$$

$$= \frac{K_{a1}K_{a2}[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]^3 + [\text{H}_3\text{O}^+]^2K_{a1} + [\text{H}_3\text{O}^+]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}}$$
(3)

$$\alpha_{PO_{4}^{3-}} = \frac{[PO_{4}^{3-}]}{P}$$

$$= \frac{K_{a1}K_{a2}K_{a3}[H_{3}PO_{4}]}{P[H_{3}O^{+}]^{3}}$$

$$= \frac{K_{a1}K_{a2}K_{a3}[H_{3}PO_{4}]}{\frac{1}{[H_{3}O^{+}]^{3}}\{[H_{3}O^{+}]^{3} + [H_{3}O^{+}]^{2}K_{a1} + [H_{3}O^{+}]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}\}[H_{3}PO_{4}][H_{3}O^{+}]^{3}}$$

$$= \frac{K_{a1}K_{a2}K_{a3}}{[H_{3}O^{+}]^{3} + [H_{3}O^{+}]^{2}K_{a1} + [H_{3}O^{+}]K_{a1}K_{a2} + K_{a1}K_{a2}K_{a3}}$$
(4)