Chemistry 201

An examination of phosphate: an important polyprotic acid

NC State University

Phosphate as a polyprotic acid

Phosphate has three acidic hydrogens. In such cases, we define the various K_a's with numbers K_{a1}, K_{a2}, etc.

$$H_3PO_4 + H_2O \rightarrow H_2PO_4^- + H_3O^+ \quad K_{a1}$$

$$H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+ \quad K_{a2}$$

$$HPO_4^{2-} + H_2O \rightarrow PO_4^{3-} + H_3O^+ \quad K_{a3}$$

$$K_{a1} = 7.25 \text{ x } 10^{-3}$$

$$K_{a2} = 6.31 \text{ x } 10^{-8}$$

$$K_{a3} = 4.80 \text{ x } 10^{-13}$$

Polyprotic acid: Phosphoric acid

Let's examine a 1 M solution of phosphoric acid.

$$H_3PO_4 \leftrightarrow H_2PO_4^- + H^+$$

The equilibrium constant is

$$K_{a1} = \frac{[H_2PO_4^-][H^+]}{[H_3PO_4]}$$

The appropriate ICE table is

Molecule	$[H_3PO_4]$	$[H_2PO_4^-]$	$[H^+]$
Initial	C	0	0
Difference	-x	x	x
Equilibrium	C - x	x	x

Polyprotic acid: Phosphoric acid

Here we see the full treatment including the quadratic formula

$$K_{a1} = \frac{x^2}{C - x}$$

$$x = \frac{K_a \pm \sqrt{K_a{}^2 + 4CK_a}}{-2}$$

$$x = \frac{7.1 \times 10^{-3} \pm \sqrt{(7.1 \times 10^{-3})^2 + 4(7.1 \times 10^{-3})}}{-2}$$

$$x = 0.081$$

$$pH = -log_{10}(0.081) = 1.09$$

Short cut method: does it work?

Here we see the short cut that assumes x << C.

$$K_{a1} \approx \frac{x^2}{C}$$

$$x^2 \approx CK_{a1}$$

$$x \approx \sqrt{CK_{a1}} = \sqrt{7.1 \times 10^{-3}} = 0.084$$

$$pH = -log_{10}(0.084) = 1.08$$

Both methods give the same result.

The second K_a equilibrium

$$H_2PO_4^{\ -} \leftrightarrow HPO_4^{\ 2-} + H^+$$

$$K_{a2} = \frac{[HPO_4^{\ 2-}][H^+]}{[H_2PO_4^{\ -}]} \qquad K_{a2} = \frac{Hx}{D - x}$$

To keep it general we designate two constants D and H.

Molecule	$[H_2PO_4^{\ -}]$	$[HPO_4^{\ 2-}]$	$[H^+]$
Initial	D	0	H
Difference	-x	x	0
Equilibrium	D - x	x	H

Here D = H = 0.084 from first Ka calculation.

$$x \approx \frac{DK_{a2}}{H} = K_{a2} = 6.3 \times 10^{-8}$$

$$[HPO_4^{\ 2-}] \approx 6.3 \times 10^{-8}$$

Treat as separate Equilibrium.
Ka separated by many orders of magnitude.

The third K_a equilibrium

$$HPO_4{}^{2-} \leftrightarrow PO_4{}^{3-} + H^+$$

$$K_{a3} = \frac{[PO_4{}^{3-}][H^+]}{[HPO_4{}^{2-}]}$$

$$K_{a3} = \frac{Hx}{E - x}$$

Molecule	$[HPO_4{}^{2-}]$	$[PO_4{}^{3-}]$	$[H^+]$
Initial	E	0	H
Difference	-x	x	0
Equilibrium	E - x	x	H

Here H = 0.084 from first Ka calc. and E = 6.3×10^{-8}

$$x \approx \frac{EK_{a3}}{H} = \frac{K_{a2}K_{a3}}{[OH^-]} = \frac{(6.3 \times 10^{-8})(4.5 \times 10^{-13})}{0.084}$$

$$[PO_4{}^{3-}] \approx 3.6 \times 10^{-19}$$

Analysis

In considering the polyprotic acid equilibria of phosphate
We have the following key points.

1. The first equilibrium can be treated as a weak acid.

2. Each equilibrium can be treated separately.

3. The first equilibrium will give the $[H^+]$ and determine the pH. Subsequent equilibrium constants are orders of magnitude smaller and will contribute a negligible amount to the pH. The pH is a constant determined by the first K_a.