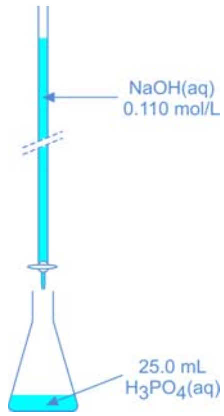
Ionic Equilibriums in Water

#6

Titration of 25.0 mL H_3PO_4-solution (with unknown concentration) with 0.110 mol/L NaOH(aq). The first equivalence point is reached after adding 26.4 mL NaOH.



1. Calculate the original H_3PO_4-concentration.
2. Calculate the pH at the start of the titration (0 mL added).
3. Calculate the pH at the first equivalence point.
4. Which volume of NaOH(aq) must be added to reach the second equivalence point.
5. Calculate the pH at the second equivalence point.

Solutions

Reaction 1: **1** H_3PO_4(aq) + **1** NaOH(aq) $\longrightarrow$ H_2O + NaH_2PO_4(aq)

1. At the first EP the total amount of H_3PO_4 has reacted and is converted into NaH_2PO_4.

   26.4 mL 0.110 mol/L NaOH(aq) contains $26.4\times10^{-3}\,\text{L}\times0.110\,\frac{\text{mol}}{\text{L}}=2.90\times10^{-3}\,\text{mol}$ of NaOH.

   So the original H_3PO_4-solution also contained 2.90×10^{-3} mol of H_3PO_4.

   The unknown H_3PO_4-concentration was $\frac{2.90\times10^{-3}\,\text{mol}}{25.0\times10^{-3}\,\text{L}}=0.116\,\frac{\text{mol}}{\text{L}}$.

2. At the start we have a H_3PO_4-solution 0.116 mol/L.

   H_3PO_4 is a rather weak acid, partially reacting with water:

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

   The second step can be neglected!

mol/L	H_3PO_4	H^+	$H_2PO_4^-$
Before reaction	0.116	0	0
Δ	−x	+x	+x
After reaction	0.116 – x	x	x

$$K_{a1_{H_3PO_4}}=\frac{[H^+]\times[H_2PO_4^-]}{[H_3PO_4]}=7.5\times10^{-3}$$

$$\frac{x^2}{0.116-x}=7.5\times10^{-3}$$

$$x^2+7.5\times10^{-3}x-8.7\times10^{-4}=0$$

$$x=0.026$$

mol/L	HOAc	H^+	OAc^-
After reaction	0.090	0.026	0.026

pH = −log 0.026 = 1.59.

3. After adding 26.4 mL NaOH (first EP), containing $26.4\times10^{-3}\text{L}\times0.110\ \frac{\text{mol}}{\text{L}}=2.90\times10^{-3}$ mol of NaOH:

mole	H_3PO_4	NaOH	NaH_2PO_4
Before reaction	2.90×10^{-3}	2.90×10^{-3}	0
Δ	-2.90×10^{-3}	-2.90×10^{-3}	$+2.90\times10^{-3}$
After reaction	0	0	2.90×10^{-3}

$(Na^+)H_2PO_4^-$: salt, containing the ampholyte $H_2PO_4^-$.

$$\begin{aligned}
\text{pH} &= \frac{1}{2}\left(\text{p}K_a + \text{p}K_a'\right)\\
&= \frac{1}{2}\left(\text{p}K_{a_{H_2PO_4^-}} + \text{p}K_{a_{H_3PO_4}}\right)\\
&= \frac{1}{2}\left(\text{p}K_{a_{2\,H_3PO_4}} + \text{p}K_{a_{1\,H_3PO_4}}\right)\\
&= \frac{1}{2}(7.21+2.12)\\
&= 4.67
\end{aligned}$$

4. If we add more NaOH when reaction 1

1 H_3PO_4(aq) + **1** NaOH(aq) ⟶ H_2O + NaH_2PO_4(aq)

is completed, reaction 2

1 NaH_2PO_4 (aq) + **1** NaOH(aq) ⟶ H_2O + Na_2HPO_4(aq)

will occur.

If we need 26.4 mL of NaOH to complete reaction 1, we will need an extra 26.4 mL to complete reaction 2.

So we will reach the second EP after adding 52.8 mL of NaOH.

5. At the second EP, the original amount of 2.90×10^{-3} mol of H_3PO_4 will be converted into 2.90×10^{-3} mol of $(Na^+)_2HPO_4^{2-}$. This salt contains the ampholyte HPO_4^{2-} .

$$\begin{aligned}
\text{pH} &= \frac{1}{2}\left(\text{p}K_a + \text{p}K_a'\right)\\
&= \frac{1}{2}\left(\text{p}K_{a_{HPO_4^{2-}}} + \text{p}K_{a_{H_2PO_4^-}}\right)\\
&= \frac{1}{2}\left(\text{p}K_{a_{3\,H_3PO_4}} + \text{p}K_{a_{2\,H_3PO_4}}\right)\\
&= \frac{1}{2}(12.65+7.21)\\
&= 9.93
\end{aligned}$$