Question

What volumes of 0.50 M HNO₂ and 0.50 M NaNO₂ must be mixed to prepare 1.00 L of a solution buffered at pH = 3.62?

Solution

pH of given buffer solution is calculated as

$$pH = pK_a + lg \frac{[NO_2^-]}{[HNO_2]}$$

For nitrous acid $pK_a = 3.39$

Thus, we have

$$3.62 = 3.39 + lg \frac{[NO_2^-]}{[HNO_2]},$$

whence

$$lg \frac{[NO_2^-]}{[HNO_2]} = 0.23$$

and

$$\frac{[NO_2^-]}{[HNO_2]} = 10^{0.23} = 1.698$$

Assuming NaNO₂ dissosiates completely, we can state $[NO_2^-]$ = $[NaNO_2]$

The concentrations of NaNO₂ and HNO₂ in the buffer solution are related to the concentrations of initial solutions ($[NO_2^-]_0$ and $[HNO_2]_0$) as follows

$$[NO_2^-] = \frac{[NO_2^-]_0 \cdot V_{(NaNO_2)}}{V_{hs}} = \frac{0.50 \cdot V_{(NaNO_2)}}{1.00} = 0.50 \cdot V_{(NaNO_2)}$$

$$[HNO_2] = \frac{[HNO_2]_0 \cdot V_{(HNO_2)}}{V_{bs}} = \frac{0.50 \cdot V_{(HNO_2)}}{1.00} = 0.50 \cdot V_{(HNO_2)},$$

where $V_{(NaNO_2)}$ and $V_{(HNO_2)}$ - volumes of the initial solutions, V_{bs} - volume of resulting buffer solution.

We know that

$$V_{(NaNO_2)} + V_{(HNO_2)} = V_{bs} = 1.00$$

We have also calculated that

$$\frac{[NO_2^-]}{[HNO_2]} = \frac{0.50 \cdot V_{(NaNO_2)}}{0.50 \cdot V_{(HNO_2)}} = \frac{V_{(NaNO_2)}}{V_{(HNO_2)}} = 1.698$$

Let us assign $V_{(NaNO_2)} = x$ and $V_{(HNO_2)} = y$

We have the set of two equations with two unknown values:

$$\begin{cases} x + y = 1.00 \\ \frac{x}{y} = 1.698 \end{cases}$$

$$x = 1.698 \cdot y$$

$$1.698 \cdot y + y = 1.00$$

$$2.698 \cdot y = 1.00$$

$$y = \frac{1.00}{2.698} = 0.37$$

$$x = 1.00 - y = 1.00 - 0.37 = 0.63$$

Answer:
$$V_{(NaNO_2)} = 0.63 L$$

 $V_{(HNO_2)} = 0.37 L$