## Preparation of Buffer Solutions by Different Laboratory Ways

## Dissociation of triprotic acid:

$\square$ Triprotic acid is acid that contain three hydrogens ions.

- It dissociates in solution in three steps, with three Ka values.
$\square$ phosphoric acid is an example of triprotic acid.
- It dissociates in solution as following:

$$
\begin{array}{ll}
\mathrm{H}_{3} \mathrm{PO}_{4} \leftrightharpoons \mathrm{H}^{+}+\mathrm{H}_{2} \mathrm{PO}_{4}^{-} & \mathrm{pK}_{1}=2.12 \\
\mathrm{H}_{2} \mathrm{PO}_{4}^{-} & \leftrightharpoons \mathrm{H}^{+}+\mathrm{HPO}_{4}^{2-} \\
\mathrm{HPO}_{4}{ }^{2-} & \mathrm{pK}_{2}=7.21 \\
\mathrm{H}^{+}+\mathrm{PO}_{4}^{3-} & \mathrm{pK}_{3}=12.30
\end{array}
$$

Note: $\mathrm{Ka}_{1}>\mathrm{Ka}_{2}>\mathrm{Ka}_{3}$ Always true for polyprotic acids

## Preparation of buffer by several ways:

- For example if you was asked to prepare sodium phosphate buffer $\left[\mathrm{NaH}_{2} \mathrm{PO}_{4} / \mathrm{Na}_{2} \mathrm{HPO}_{4}\right]$ : you can prepare it by........

1. By mixing $\mathrm{NaH}_{2} \mathrm{PO}_{4}$ (conjugate acid ) and $\mathrm{Na}_{2} \mathrm{HPO}_{4}$ (conjugate base) in the proper proportions.
2. By starting with $\underline{H}_{3} \mathrm{PO}_{4}$ and converting it to $\mathrm{Na}_{2} \underline{H}_{2} \mathrm{PO}_{4}$ plus $\mathrm{Na}_{2} \mathrm{HPO}_{4}$ by adding the proper amount of $\mathbf{N a O H}$.
3. By starting with $\mathrm{Na}_{2} \underline{H}_{2} \mathrm{PO}_{4}$ and converting a portion of it to $\mathrm{Na}_{2} \underline{\mathrm{HPO}_{4}}$ by adding $\mathbf{N a O H}$.
4. By starting with $\mathrm{Na}_{2} \underline{\mathrm{HPO}_{4}}$ and converting a portion of it to $\mathrm{Na}_{2} \mathrm{PO}_{4}$ by adding a strong acid such as HCL.
5. By starting with $\mathrm{Na}_{3} \mathrm{PO}_{4}$ and converting it to $\mathrm{Na}_{2} \mathrm{HPO}_{4}$ plus $\mathrm{NaH}_{2} \mathrm{PO}_{4}$ by adding HCL.
6. By mixing $\mathrm{Na}_{3} \mathrm{PO}_{4}$ and $\mathrm{NaH}_{2} \mathrm{PO}_{4}$ in the proper proportions.

##  <br> $\mathrm{HPO}_{4}{ }^{2-}$ <br> $\mathrm{PO}_{4}{ }^{3-}$ <br> ${ }^{\prime}$ accept $\mathbf{H}^{+}$,

b) From solid $\mathrm{NaH}_{2} \mathrm{PO}_{4}$ and solid NaOH .

## Calculations:

$1^{\text {st }} \rightarrow$ Write the equations of phosphoric acid dissociation and the pKa of corresponding ones:

Regardless of which method is used, the first step involves determine the buffer ionic species, calculating number of moles and amounts of the two ionic species in the buffer. Because phosphoric acid $\left[\mathrm{H}_{3} \mathrm{PO}_{4}\right]$ is triprotic acid it has 3 dissociation phases so:

$$
\begin{array}{ll}
\mathrm{H}_{3} \mathrm{PO}_{4} \leftrightharpoons \mathrm{H}^{+}+\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-} & \mathrm{pK}_{1}=2.12 \\
\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-} \leftrightharpoons \mathrm{H}^{+}+\mathrm{HPO}_{4}{ }^{2-} & \mathrm{pK}_{\mathbf{2}}=7.21 \\
\mathrm{HPO}_{4}{ }^{2-} \leftrightharpoons \mathrm{H}^{+}+\mathrm{PO}_{4}{ }^{3-} & \mathbf{p K}_{3}=12.30
\end{array}
$$

$2^{\text {nd }} \rightarrow$ Choose the pKa value which is near the pH value of the required buffer, to be able to know the ionic species involved in your buffer:

$$
\mathrm{H}_{3} \mathrm{PO}_{4} \leftrightharpoons \mathrm{H}^{+}+\mathrm{H}_{2} \mathrm{PO}_{4}^{-} \quad \mathrm{pK}_{1}=2.12
$$

| $\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-} \leftrightharpoons \mathrm{H}^{+}+\mathrm{HPO}_{4}{ }^{2 \cdot}$ | $\mathrm{pK}_{2}=7.21$ |
| :--- | :--- |
| $\mathrm{HPO}_{4}{ }^{2}{ }^{-} \leftrightharpoons \mathrm{H}^{+}+\mathrm{PO}_{4}{ }^{3 \cdot}$ | $\mathrm{pK}_{3}=12.30$ |

$\rightarrow$ The pH of the required buffer $[\mathrm{pH}=7.5]$ is near the value of pKa 2 , consequently, the two major ionic species present are $\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}$( conjugate acid ) and $\mathrm{HPO}_{4}{ }^{2-}$ (conjugate base), with the $\mathbf{H P O}_{4}{ }^{2-}$ predominating \{since the pH of the buffer is slightly basic\}.

## Calculations cont':

$3^{\text {rd }} \rightarrow$ calculate No. of moles for the two ionic species in the buffer:
$\mathbf{p H}=\mathbf{p K a} \mathbf{2}+\log \left[\mathbf{H P O}_{\mathbf{4}^{\mathbf{2 -}}}{ }^{-}\right] /\left[\mathbf{H}_{\mathbf{2}} \mathbf{P O}_{\mathbf{4}}{ }^{-}\right] \quad \rightarrow$ Note that: $\quad\left[\mathrm{A}^{-}\right]=\mathrm{HPO}_{4}{ }^{2-}, \quad[\mathrm{HA}]=\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}$

- Since the buffer concentration is 0.045 M , so assume $\left[\mathrm{A}^{-}\right]=\mathrm{y},[\mathrm{HA}]=0.045-\mathrm{y}$ :
$7.5=7.2+\log (y / 0.045-y)$
7.5-7.2 $=\log (\mathrm{y} / 0.045-\mathrm{y})$
$0.3=\log (\mathrm{y} / 0.045-\mathrm{y}) \rightarrow$ antilog for both sides
$\boldsymbol{\rightarrow} 2=(\mathrm{y} / 0.045-\mathrm{y}) \boldsymbol{\rightarrow} \mathrm{y}=0.09-2 \mathrm{y} \boldsymbol{\rightarrow} 3 \mathrm{y}=0.09 \boldsymbol{\rightarrow} \mathrm{y}=0.9 / 3=\underline{\mathbf{0 . 0 3 M}} \boldsymbol{\rightarrow}$ conc. of $\left[\mathrm{HPO}_{4}{ }^{2-}\right]=[\mathrm{A}-]=\mathrm{y}$
So, conc. of $\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]=[\mathrm{HA}]=0.045-\mathrm{y}=0.045-0.03=\underline{\mathbf{0 . 0 1 5} \mathbf{~ M}}$
- Now find the number of mole for the two ionic species in the buffer:
- No. of moles of $=\mathrm{HPO}_{4}{ }^{2-}\left(\mathrm{A}^{-}\right)=\mathrm{M} \mathrm{x} \mathrm{V}=0.03 \times 0.1=0.003$ moles.
- No. of moles of $\mathrm{H}_{2} \mathrm{PO}_{4}^{-}(\mathrm{HA})=\mathrm{M} \mathrm{x} \mathrm{V}=0.015 \times 0.1=0.0015$ moles.
$\rightarrow$ Note that Total no. of moles of phosphate buffer $=\mathrm{MxV}=0.045 \times 0.1=0.0045$ moles.

> Now, to prepare the required buffer:
a) From concentrated (15M) $\mathrm{H}_{3} \mathrm{PO}_{4}$ and solution of 1.5 M NaOH .

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Remember that the two ionic species
involved in the buffer are:
H2}\mp@subsup{\textrm{PO}}{4}{-
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## Calculations:

Start with 0.0045 mole of $\underline{\mathbf{H}}_{3} \underline{\mathbf{P O}}_{4}$ add $\mathbf{0 . 0 0 4 5}$ moles of NaOH to convert $\underline{\mathrm{H}}_{3} \mathbf{P O}_{4}$ completely to $\underline{H}_{2} \mathrm{PO}_{4}^{-}(\mathrm{HA})$, then add 0.003 moles of NaOH to convert $\underline{\mathrm{H}}_{2} \mathrm{PO}_{4}^{-}$ to give $\underline{H P O}_{4}{ }^{2-}\left(\mathrm{A}^{-}\right)$:

No. of moles needed of $\mathrm{NaOH}=0.0045+0.003=\underline{0.0075}$ moles
$\rightarrow$ Volume of $\mathbf{N a O H}$ needed $=$ no.of moles $/ \mathrm{M}=0.0075 / 1.5=0.005 \mathrm{~L}=5 \mathrm{ml}$
$\rightarrow$ Volume of $\mathbf{H}_{3} \mathbf{P O} 4$ needed $=$ no.of moles $/ \mathrm{M}=0.0045 / 15=0.0003 \mathrm{~L}=\underline{0.3 \mathrm{ml}}$


Add $\mathbf{5 m l}$ of NaOH to the $\mathbf{0 . 3} \mathbf{~ m l}$ of concentrate $\mathrm{H}_{3} \mathrm{PO}_{4}$, mix ; then add sufficient water to bring the final volume to 0.1 liters $(100 \mathrm{ml})$, and check the pH .
b) From solid $\mathrm{NaH}_{2} \mathrm{PO}_{4}$ and solid NaOH .

## Calculations:

Start with 0.0045 mole of $\mathrm{NaH}_{2} \mathrm{PO}_{4}(\mathrm{HA})$ and add 0.003 moles of NaOH to convert $\mathrm{NaH}_{2} \mathrm{PO}_{4}$ to give $\mathrm{Na}_{2} \mathrm{HPO}_{4}\left(\mathrm{~A}^{-}\right):$
$\rightarrow$ Weight in grams of $\mathbf{N a H}_{2} \mathbf{P O}_{4}$ needed $=$ no. of moles $\times \mathrm{MW}=0.0045 \times 119.98=\underline{0.54 \mathrm{~g}}$
$\rightarrow$ Weight in grams of $\mathbf{N a O H}$ needed $=$ no. of moles $\times \mathrm{MW}=0.003 \times 40=\underline{0.12 \mathrm{~g}}$
So: Dissolve the 0.548 g of $\mathbf{N a H}_{2} \mathbf{P O}_{4}$ and 0.12 g of $\mathbf{N a O H}$ in some water, mix ; then add sufficient water to bring the final volume to 0.1 liters ( 100 ml ), and check the pH .

Remember that the two ionic species involved in the buffer are:

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## Objective:

$\square$ To learn how to prepare a buffer by different laboratory ways.

## Method:

$\square$ Prepare 0.1 liters of $\mathbf{0 . 0 4 5} \mathrm{M}$ sodium phosphate buffer, $\mathbf{p H}=7.5$, $[p K a 1=2.12, p K a 2=7.21$ and $p K a 3=12.30]:$
a) From concentrated (15M) $\mathrm{H}_{3} \mathrm{PO}_{4}$ and solution of 1.5 M NaOH :

Add $\mathbf{5 m l}$ of $\mathbf{N a O H}$ to the $\mathbf{0 . 3} \mathbf{~ m l}$ of concentrate $\mathbf{H}_{\mathbf{3}} \mathbf{P O}_{\mathbf{4}}$, mix ; then add sufficient water to bring the final volume to 0.1 liters ( 100 ml ), and check the pH .
b) From solid $\mathrm{NaH}_{2} \mathrm{PO}_{4}$ and solid NaOH :

Dissolve the $\mathbf{0 . 5 8 4 g}$ of $\mathbf{N a H}_{2} \mathbf{P O}_{4}$ and 0.12 g of $\mathbf{N a O H}$ in some water, mix ; then add sufficient water to bring the final volume to 0.1 liters $(100 \mathrm{ml})$, and check the pH .

## Homework

$\square$ Prepare 0.1 liters of $\mathbf{0 . 0 4 5} \mathrm{M}$ sodium phosphate buffer, $\mathbf{p H}=7.5$, $[p k a 1=2.12, p k a 2=7.21$ and pka3 = 12.30]:

You are provided with solid Na3PO4 and 2 M HCL .

