## Objectives



At the end of this unit, the student is expected to be able to :
1- Understand the concept of the buffer, its importance in chemistry and in real life and its types.
2- Realize the way by which the buffer stabilizes the pH .
3 - Calculate the pH of all sorts of buffer solutions.
4- Know how to prepare all types of buffer solutions .
5- Recognize the role of polyprotic acids in the preparation of buffer solutions .

## Introduction

A buffer is an aqueous solution consisting of a mixture of a weak acid and its salt ( acidic buffer ) or a weak base and its salt ( basic buffer ). Its pH changes very little when a small amount of strong acid or base is added to it and thus it is used to prevent changes in the pH of a solution.

Buffer solutions are used in a wide variety of chemical applications. One example of a buffer solution found in nature is blood. The normal pH of human blood is 7.4. Some people suffer from alkalosis when experiencing severe anxiety. Alkalosis is a condition in which the pH of the blood is too high. The opposite condition - a blood pH lower than 7.4 is called acidosis .

Some chemical reactions proceed only at a certain pH . Many household and cosmetic products need to control their pH values such as, shampoo to counteract the alkalinity of the soap and prevent irritation, baby lotion to maintain a pH of about 6 to prevent bacteria multiplying, washing powder, eye drops, fizzy lemonade .....etc .

## Types of Buffer Solutions

## Acidic buffer solutions :

An acidic buffer solution is simply one which has a pH less than 7 . Acidic buffer solutions are commonly made from a weak acid and one of its salts - often a sodium salt.
A common example would be a mixture of acetic acid and sodium acetate in solution. You can change the pH of the buffer solution by changing the ratio of acid to salt, or by choosing a different acid and one of its salts.


## Types of Buffer Solutions

## Alkaline ( basic ) buffer solutions

An alkaline buffer solution has a pH greater than 7. Alkaline buffer solutions are commonly made from a weak base and one of its salts. A frequently used example is a mixture of ammonia solution and ammonium chloride solution. A buffer solution has to contain things which will remove any hydrogen ions or hydroxide ions that you might add to it - otherwise the pH will change. Acidic and alkaline buffer solutions achieve this in different ways.

## How do buffers work?

## Acidic buffer solutions

We'll take a mixture of acetic acid and sodium acetate as typical. Acetic acid is a weak acid, and the position of this equilibrium will be well to the left :


Adding sodium acetate to this adds lots of extra acetate ions. According to Le Chatelier's Principle,, that will tip the position of the equilibrium even further to the left ( common ion effect ). The solution will therefore contain these important things:

- lots of un-ionised acetic acid;
- lots of acetate ions from the sodium acetate;
- enough hydrogen ions to make the solution acidic.


## How do buffers work?

Other things (like water and sodium ions) which are present aren't important to the argument.

## Adding an acid to this buffer solution :

The buffer solution must remove most of the new hydrogen ions otherwise the pH would drop markedly. Hydrogen ions combine with the acetate ions to make acetic acid.

$$
\mathrm{CH}_{3} \mathrm{COO}_{(a q)}^{\circ}+\mathrm{H}^{+}(\text {aq }) \longrightarrow \mathrm{CH}_{3} \mathrm{COOH}_{(a q)}
$$

That means a strong acid has been turned to a weak acid. Since most of the new hydrogen ions are removed, the pH won't change very much - but because of the equilibrium involved, it will fall a little bit.

## How do buffer work?

Adding a base to this buffer solution
Alkaline solutions contain hydroxide ions and the buffer solution removes most of these by reacting with $H^{+}$to form water. As soon as this happens, the equilibrium of the acid dissociation tips to replace $\mathrm{H}^{+}$ions. This keeps on happening until most of the hydroxide ions are removed. That means a strong base has been turned to water .


## How do buffer work?

Because most of the added hydroxide ions are removed by this way, the pH doesn't increase very much

## Alkaline ( basic ) buffer solutions

 We'll take a mixture of ammonia and ammonium chloride solutions as typical. Ammonia is a weak base, and the position of this equilibrium will be well to the left:Adding ammonium chloride to this adds lots of extra ammonium ions. According to Le Chatelier's Principle, that will tip the position of the equilibrium even further
 to the left ( common ion effect )

## How do buffers work?

The solution will therefore contain these important things:

- lots of unreacted ammonia;
- lots of ammonium ions from the ammonium chloride;
- enough hydroxide ions to make the solution alkaline.
Other things (like water and chloride ions) which are present aren't important to the argument.


## How do buffers work?

Adding an acid to this buffer solution
the hydrogen ions that you are adding are removed by reacting with OH ( see previous equation) to form water. That means a strong acid has been turned to water .


This keeps on happening until most of thehydrogen ions are removed.

## How do buffers work?

Adding a base to this buffer solution
The hydroxide ions from the alkali are removed by a simple reaction with ammonium ions.

$$
\mathrm{NH}_{4}+(a q]+\mathrm{OH}_{[a q]} \longrightarrow \mathrm{NH}_{3}(a q]+\mathrm{H}_{2} \mathrm{O}_{[\mid(\mid)}
$$

That means a strong base has been turned to a weak base. The figure on the left summarizes the mechanism by which the buffer stabilize the pH and the following table shows some common acids and bases used for the preparation of buffer solutions .

## How do buffers work?

Some common weak acids and bases and their salts usually used for the preparation of buffer solutions .

| Acid or base | salt |
| :---: | :---: |
| Acetic acid | Sodium acetate |
| Phosphoric acid | Potassium phosphate |
| Oxalic acid | Lithium oxalate |
| Carbonic acid | Sodium carbonate |
| Ammonia | Ammonium chloride |

## Buffer Solution's Calculations

## Acidic buffer solutions

This is easier to see with a specific example. Let's suppose that you had a buffer solution containing 0.10 M of acetic acid and 0.20 M of sodium acetate. How do you calculate its pH ? In any solution containing a weak acid, there is an equilibrium between the un-ionized acid and its ions. So for acetic acid, you have the equilibrium :

$$
\left.\mathrm{CH}_{3} \mathrm{COOH}_{(a q]} \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}_{[\mathrm{aq}]}\right)+\mathrm{H}^{+}[\mathrm{aq}]
$$

## CHEM I180- Lecture 031

pH OF A BUFFER SOLUTION ON ADDITION OF A
STRONG ACID OR BASE

1. A buffer is made by combining 55.0 mL of 0.450 M HF and 45.0 mL of 0.250 M NaF at $25^{\circ} \mathrm{C} .95 .0 \mathrm{~mL}$ of this buffer is mived with 5.00 mL of 0.100 M HCL . What is new pll?

## Buffer Solution's Calculations

The presence of the acetate ions from the sodium acetate will have moved the equilibrium to the left, but the equilibrium still exists.
That means that you can write the equilibrium constant, $\mathrm{K}_{\mathrm{a}}$, for it:

$$
K_{a}=\frac{\left.\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right] \mathrm{LH}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}
$$

## VIDEO

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VIDEO
pH of a buffer

Where you have done calculations using this equation previously with a weak acid, you will have assumed that the concentrations of the hydrogen ions and acetate ions were the same.

## Buffer Solution's Calculations

Every molecule of acetic acid that splits up gives one of each sort of ion.That's no longer true for a buffer solution :

```
These two ions are no longer equal
    Ka}=\frac{[\mp@subsup{\textrm{CH}}{3}{}\mp@subsup{\textrm{COO}}{}{-}][\mp@subsup{H}{}{+}]}{[\mp@subsup{\textrm{CH}}{3}{}\textrm{COOH}]
```

If the equilibrium has been pushed even further to the left, the number of acetate ions coming from the acetic acid will be completely negligible compared to those from the sodium acetate.

We therefore assume that the acetate ion concentration is the same as the concentration of the sodium acetate - in this case, $0.20 \mathrm{~mol} / \mathrm{L}$.

## Buffer Solution's Calculations

In a weak acid calculation, we normally assume that so little of the acid has ionised that the concentration of the acid at equilibrium is the same as the concentration of the acid we used. That is even more true now that the equilibrium has been moved even further to the left. So the assumptions we make for a buffer solution are :

```
Assume this is the same as the
concentration of the sodium acetate
    Ka}=\frac{[\mp@subsup{\textrm{CH}}{3}{}\mp@subsup{\textrm{COOO}}{}{-}][\mp@subsup{H}{}{+}]}{[CH3COOOH]
        4
Assume this is the same as the
concentration of the original acid
```

Now, if we know the value for $K_{a}$, we can calculate the hydrogen ion concentration and therefore the $\mathrm{pH} . \mathrm{K}_{\mathrm{a}}$ for acetic acid is $1.74 \times 10^{-5}$.

## Buffer Solution's Calculations

Remember that we want to calculate the pH of a buffer solution containing 0.10 M of acetic acid and 0.20 M of sodium acetate .

$$
\begin{aligned}
K_{a} & =\frac{\left[\mathrm{CH}_{3} \mathrm{COOH}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]} \\
1.74 \times 10^{-5} & =\frac{0.2 \times\left[\mathrm{H}^{+}\right]}{0.10} \\
{\left[\mathrm{H}^{+}\right] } & =1.74 \times 10^{-5} \times \frac{0.10}{0.20} \\
& =8.7 \times 10^{-6} \mathrm{~mole} / \mathrm{L}
\end{aligned}
$$

Then all you have to do is to find the pH using the expression :

$$
\mathrm{pH}=-\log _{10}\left[\mathrm{H}^{+}\right]=-\log 8.7 \times 10^{-6}=5.1
$$

## Buffer Solution's Calculations

You could, of course, be asked to reverse this and calculate in what proportions you would have to mix acetic acid and sodium acetate to get a buffer solution of some desired pH . It is no more difficult than the calculation we have just looked at. Suppose you wanted a buffer with a pH of $4.46\left(\right.$ i.e $\left[\mathrm{H}^{+}\right]=$shift $\left.\log -4.46=3.47 \mathrm{X} 10^{-5} \mathrm{M}\right)$. Feed that into the $\mathrm{K}_{\mathrm{a}}$ expression :

$$
\begin{aligned}
& K_{a}=\frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}^{2}\right]} \\
& 1.74{\mathrm{X} 10^{-5}}^{=} \frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right] \mathrm{X} 3.47 \times 10^{-5}}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]} \\
& \frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}=\frac{1.74 \times 10^{-5}}{3.47 \times 10^{-5}}=0.50
\end{aligned}
$$

## Buffer Solution's Calculations

All this means is that to get a solution of pH 4.46 , the concentration of sodium acetate has to be have that of acetic acid. In general we can use the following equations for calculating a pH of any buffer :

$$
\begin{array}{cccc}
\mathrm{HA} & \leftrightarrow & \mathrm{~A}^{-} & + \\
\mathrm{C}_{\mathrm{a}}^{-}- & \mathrm{H}^{+} & \mathbf{x} & \mathbf{x} \\
\mathrm{NaA} & \rightarrow & \mathrm{~A}^{-}+ & \mathrm{Na}^{+} \\
0 & & \mathrm{C}_{\mathrm{s}} & \mathrm{C}_{\mathrm{s}}
\end{array}{ }^{K_{a}=} \frac{\left[H^{+}\right]\left[A^{-}\right]}{[H A]}=\frac{\left[H^{+}\right]\left(C_{s}+x\right)}{C_{a}-x} \cong \frac{\left[H^{+}\right] C_{s}}{C_{a}} .
$$

Multiplying both sides by $-\log$ we obtain what is called Henderson-Hasselbalch equation :

## Buffer Solution's Calculations

$$
p H=p K_{a}+\log \frac{C_{s}}{C_{a}}
$$

Where HA is the weak acid , $\mathrm{C}_{\mathrm{a}}$ is its initial concentration, NaA is the sodium salt of the weak acid, $\mathrm{C}_{\mathrm{s}}$ is the concentration of the salt. Note that :

$$
\left[\mathrm{A}^{-}\right]=\mathrm{C}_{\mathrm{s}}+\mathrm{x} \cong \mathrm{C}_{\mathrm{s}}
$$

The above equation is the general equation used for calculation of a pH of a buffer composed of a weak acid and its salt .

Calculate the pH of a buffer system
Calculate the pH of a buffer solution that is $0.15 \mathrm{M} \mathrm{HNO}_{2}(\mathrm{aq})$ and $0.2 \mathrm{M} \mathrm{NaNO}_{2}$.

## Buffer Solution's Calculations

## Alkaline (basic ) buffer solutions

We are talking here about a mixture of a weak base and one of its salts - for example, a solution containing ammonia and ammonium chloride .The modern, and easy, way of doing these calculations is to re-think them from the point of view of the ammonium ion rather than of the ammonia solution. Once you have taken this slightly different view-point, everything becomes much the same as before. So we will use the general following equation :

$$
\begin{aligned}
& p O H=p K_{b}+\log \frac{C_{s}}{C_{b}} \\
& p H=14-p O H
\end{aligned}
$$

```
Calculate the pH of a buffer
solution that is }0.115\mp@subsup{\textrm{m NH}}{3}{}\not=0.120\textrm{M
                                    NH4Cl
```

                                    My Channel
    
## Buffer Capacity

Where $\mathrm{C}_{\mathrm{s}}$ is the concentration of weak base salt , $\mathrm{C}_{\mathrm{b}}$ is the concentration of the weak base and $\mathrm{K}_{\mathrm{b}}$ is the dissociation constant of the weak base .
So how would you find the pH of a solution containing 0.10 M of ammonia and 0.05 M of ammonium chloride? $\mathrm{K}_{\mathrm{b}}\left(\mathrm{NH}_{3}\right)=1.8 \times 10^{-5}$ :

$$
p O H=-\log 1.8 \times 10^{-5}+\log \frac{o .05}{0.10}=4.44
$$

## Buffer Capacity :

$$
p H=14-4.44=9.56
$$

It is the number of moles or mmoles of a strong base ( y ), which when added to one liter of a buffer raises his own pH by one unit, or it is the number of moles or mmoles of a strong acid ( x ) which, when added to one liter of this buffer reduced its pH by one unit. The higher the capacity the higher the amounts of a strong acid or a strong base which can be added to the buffer without significantly changing his own pH . The capacity of a buffer solution can be increased by increasing both $\mathrm{Cs}, \mathrm{Ca}$ and Cb and it will be at maximum when $\mathrm{Cs}=\mathrm{Ca}$ or $\mathrm{Cs}=\mathrm{Cb}$ and in this case :

## Buffer Capacity

$$
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+0 \text { Or } \mathrm{pOH}=\mathrm{pK}_{\mathrm{b}}+0
$$

How to select the appropriate buffer :
In order to prepare a buffer solution at certain pH with highest capacity, you will choose the weak acid which its $\mathrm{pK}_{\mathrm{a}}$ is the nearest to the pH of the buffer or choose the weak base which its $\mathrm{pK}_{\mathrm{b}}$ is the nearest to ( $14-\mathrm{pH}$ ) of the buffer ( see tutorial exercises ).

## Buffer Capacity

Example : Calculate the buffer capacity of a buffer solution containing $0.2 \mathrm{M} \mathrm{NH}_{3}$ and 0.1 $\mathrm{M} \mathrm{NH} 44\left[\mathrm{pK}_{\mathrm{b}}\left(\mathrm{NH}_{3}\right)=4.76\right]$ ?

Solution : First : we calculate the pH of the buffer :

$$
\begin{aligned}
& \mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \stackrel{\mathrm{NH}_{4}^{+}+\mathrm{OH}^{-}}{\mathrm{NH}_{4} \mathrm{Cl}} \stackrel{\mathrm{NH}_{4}^{+}}{ }+\mathrm{Cl}^{-} \\
& p O H=4.76+\log \frac{0.1(\text { moles } / L)}{0.2(\text { moles } / L)}=4.5 \\
& \therefore p H=14-4.5=9.5
\end{aligned}
$$

## Buffer Capacity

Second : we calculate the buffer capacity by one of two ways :
(1) according to the above buffer capacity definition, suppose that x moles of strong acid such as HCl ( buffer capacity ) have been added to one liter of the buffer solution. HCl will covert the base $\mathrm{NH}_{3}$ to salt $\left(\mathrm{NH}_{4}{ }^{+}\right)$, so , the base will decrease and the salt will increase by the same number of HCl moles ( all reactions are $1: 1$ ) and the pH of the buffer will decrease by one to become 8.5 instead of 9.5 ( or the pOH will increase by one to become 5.5 instead of 4.5 ) thus :

$$
\begin{aligned}
& 5.5=4.76+\log \frac{(0.1+x) \text { moles } / L}{(0.2-x) \text { moles } / L} \\
& \therefore x=0.15(\text { moles } H C l / L)
\end{aligned}
$$

## Buffer Capacity

(2) Suppose that Y moles of strong base such as NaOH ( buffer capacity ) have been added to one liter of the buffer solution. NaOH will covert the salt $\left(\mathrm{NH}_{4}{ }^{+}\right)$into base $\mathrm{NH}_{3}$, so , the base will increase and the salt will decrease by the same number of NaOH moles ( all reactions are $1: 1$ ) and the pH of the buffer will increase by one to become 10.5 instead of 9.5 ( or the pOH will decrease by one to become 3.5 instead of 4.5 ) thus :

$$
\begin{aligned}
& 3.5=4.76+\log \frac{(0.1-y) \text { moles } / l}{(0.2+y) \text { moles } / l} \\
& \therefore y=0.08 \text { (moles NaOH } / l)
\end{aligned}
$$

We can treat a buffer consisting from a weak acid and its salt in the same above manner ( see tutorial ).

## Buffer Capacity

Example : Calculate the change in pH of 10 mL solution of a buffer containing o. 2 M of acetic acid and 0.2 M sodium acetate when 1.0 mL of 0.1 M HCl solution is added to it ? $\mathrm{pK}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=4.76$
Solution : Note that HCl will convert the acetate to acetic acid. Before adding HCl :


$$
p H=4.76+\log \frac{0.2}{0.2}=4.76
$$

After adding HCl :

$$
p H=4.76+\log \frac{(0.2 \times 10-1 X 0.1) / 11}{(0.2 \times 10+1 X 0.1) / 11}=4.71
$$

Notice the insignificant change in pH due to the buffer resistance .

## Preparation of Buffer's Solution

The methods of preparing buffer solutions Can be summarized as follows :
1- Calculating $\frac{C_{s}}{C_{a}}$ or $\frac{C_{s}}{C_{b}}$
using the previous equations and then weighing the amount of the weak acid and its salt $\left(\mathrm{C}_{\mathrm{a}}: \mathrm{C}_{\mathrm{s}}\right)$ or the amount of the weak base and its salt ( $\mathrm{C}_{\mathrm{s}}: \mathrm{C}_{\mathrm{b}}$ ) and dissolve and dilute to the appropriate volume. This method is tedious and time consuming.


## Preparation of Buffer's Solution



2- Adding drops of a strong base such as NaOH to an excess of a weak acid such as HA during which measure the pH of the solution using a pH - meter until you reach the desired pH . The added NaOH is completely turned to $\mathrm{C}_{\mathrm{s}}$ which will form with the remaining weak acid $\mathrm{C}_{\mathrm{a}}$ an acidic buffer solution :
drops of $\mathrm{NaOH}+$ excess $\mathrm{HA} \leftrightarrow \mathrm{NaA}+\mathrm{H}_{2} \mathrm{O}$
0
$C_{a}$
$C_{s}$

Unit 5

## Preparation of Buffer's Solution



## Preparation of Buffer's Solution

3- Like wise, adding drops of a strong acid such as HCl to an excess of a weak base such as $\mathrm{NH}_{3}$ will produce a basic buffer solution :

$$
\text { drops of } \mathrm{HCl}+\text { excess } \mathrm{NH}_{3} \quad \leftrightarrow \quad \mathrm{NH}_{4} \mathrm{Cl}
$$

4- Adding drops of a strong base such as NaOH to an excess of a salt of a weak base such as $\mathrm{NH}_{4} \mathrm{Cl}$ will produce a basic buffer solution :

$$
\text { drops of } \mathrm{NaOH}+\text { excess } \mathrm{NH}_{4} \mathrm{Cl} \leftrightarrow \mathrm{NH}_{3}+\mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}
$$

5- Adding drops of a strong acid such as HCl to an excess of a salt of a weak acid such as NaA will produce An acidic buffer solution

$$
\text { drops of } \mathrm{HCl}+\text { excess } \mathrm{NaA} \leftrightarrow \mathrm{HA}+\mathrm{NaCl}
$$

## Polyprotic Acids And Its Salts

Polyprotic acids are specific acids that are capable of losing more than a single proton per molecule in acid-base reactions. In other words, acids that have more than one ionizable $\mathrm{H}^{+}$atom per molecule. Protons are lost through several stages (one at each stage), with the first proton being the fastest and most easily lost. The following table, shows some of the common polyprotic acids.Note that $\mathrm{K}_{\mathrm{a} 1}>\mathrm{K}_{\mathrm{a} 2}>\mathrm{K}_{\mathrm{a} 3}$ for all polyprotic acids so $K_{a 3}$ is very small and can be neglected .

| Some Polyprotic Acids |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| Formula | Name | $\mathrm{K}_{\mathrm{a} 1}$ | $\mathrm{~K}_{\mathrm{a} 2}$ | $\mathrm{~K}_{\mathrm{a} 3}$ |
| $\mathbf{H}_{2} \mathbf{S}$ | Hydrogen <br> sulfide | $1.0 \mathrm{E}-7$ | $1 \mathrm{E}-19$ |  |
| $\mathbf{H}_{\mathbf{2}} \mathbf{S O}_{4}$ | Sulfuric acid | Very Large | $1.1 \mathrm{E}-2$ |  |
| $\mathbf{H}_{\mathbf{2}} \mathbf{S O}_{\mathbf{3}}$ | Sulfurous acid | $1.3 \mathrm{E}-2$ | $6.2 \mathrm{E}-8$ |  |
| $\mathbf{H}_{3} \mathbf{P O}_{\mathbf{4}}$ | Phosphoric <br> acid | $7.1 \mathrm{E}-3$ | $6.3 \mathrm{E}-8$ | $4.2 \mathrm{E}-13$ |
| $\mathbf{H}_{\mathbf{2}} \mathbf{C}_{\mathbf{2}} \mathbf{O}_{\mathbf{4}}$ | Oxalic acid | $5.4 \mathrm{E}-2$ | $5.3 \mathrm{E}-5$ |  |
| $\mathbf{H}_{\mathbf{2}} \mathbf{C O}_{\mathbf{3}}$ | Carbonic acid | $4.4 \mathrm{E}-7$ | $4.7 \mathrm{E}-11$ |  |
| $\mathbf{H}_{\mathbf{2}} \mathbf{C}_{\mathbf{3}} \mathbf{H}_{\mathbf{2}} \mathbf{O}_{\mathbf{4}}$ | Malonic acid | $1.5 \mathrm{E}-3$ | $2.0 \mathrm{E}-6$ |  |

## Polyprotic Acids And Its Salts

Calculation of pH of a polyprotic acid solution :
1- If $K_{a 1}>K_{a 2}$, then the polyprotic acid solution can be treated as a monoprotic acid thus :

$$
p H=-\log \sqrt{K_{a_{1}} \cdot c_{a}}
$$

2- If $\mathrm{K}_{\mathrm{a} 1}>\mathrm{K}_{\mathrm{a} 2} \times 10^{2}$, then we consider the first ionization stage is complete and we use only the second ionization stage thus :

## Polyprotic Acids And Its Salts

$$
p H=-\log \sqrt{K_{a_{2}} \cdot C_{a}}
$$

3- If $\mathrm{K}_{\mathrm{a} 1} \approx \mathrm{~K}_{\mathrm{a} 2}$ we use the following approximate equation :


$$
p H=-\log \sqrt{K_{a_{1}} \cdot K_{a_{2}}}
$$

## Polyprotic Acids And Its Salts

Let us discuss $\mathrm{H}_{3} \mathrm{PO}_{4}$ and what applies to this acid applies to all polyprotic acids except $\mathrm{H}_{2} \mathrm{SO}_{4}$ ( see ref. 1 and 5 ). The three dissociation stages of $\mathrm{H}_{3} \mathrm{PO}_{4}$ as follows :

$$
\begin{aligned}
& \mathrm{H}_{3} \mathrm{PO}_{4} \leftrightarrow \mathrm{H}_{2} \mathrm{PO}_{4}^{-}+\mathrm{H}^{+} \quad, \quad \mathrm{K}_{a_{4}}=\frac{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{H}_{3} \mathrm{PO}_{4}\right]} \\
& \mathrm{H}_{2} \mathrm{PO}_{4}^{-} \leftrightarrow \mathrm{HPO}_{4}{ }^{2-}+\mathrm{H}^{+} \quad, \quad K_{a_{4}}=\frac{\left[\mathrm{HPO}_{4}^{2-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{H}_{2} \mathrm{PO}_{4}^{-}\right]} \\
& \mathrm{HPO}_{4}{ }^{2-} \leftrightarrow \mathrm{PO}_{4}{ }^{3-}+\mathrm{H}^{+} \quad, \quad K_{a_{3}}=\frac{\left[\mathrm{PO}_{4}^{3-}\right]\left[\mathrm{H}^{+}\right]}{\left[{\mathrm{HPO}_{4}}^{2-}\right]}
\end{aligned}
$$

## Polyprotic Acids And Its Salts

Since $K_{a 1}>K_{a 2} \times 10^{2}$ ( see the previous table ), so we use the following equation for the calculation of the pH of its solution :

$$
p H=-\log \sqrt{K_{a_{2}} \cdot C_{a}}
$$

## Polyprotic Acids and Its Salts

To calculate the pH of $\mathrm{H}_{3} \mathrm{PO}_{4}$ salts we use the following approximate equations :

| salts | Approximate equations | Remarks |
| :---: | :---: | :---: |
| $\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}$ | $p H=-\log \sqrt{K_{a_{1}} \cdot K_{a_{2}}}$ | exist in first and second ionization |
| stage |  |  |

## Polyprotic Acids And Its Salts

Continues to previous table

| $\mathrm{H}_{3} \mathrm{PO}_{4}+\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}$ | $p H=p K_{a_{1}}+\log \frac{\left[\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}\right]}{\left[\mathrm{H}_{3} \mathrm{PO} \mathrm{O}_{4}\right]}$ | buffer and both exist in first <br> ionization stage |
| :---: | :---: | :---: |
| $\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}+\mathrm{HPO}_{4}{ }^{2-}$ | $p H=p K_{a_{2}}+\log \frac{\left[\mathrm{HPO}_{4}{ }^{2-}\right]}{\left[\mathrm{H}_{2} \mathrm{PO}_{4}{ }^{-}\right]}$ | Buffer and both exist in second <br> ionization stage |
| $\mathrm{HPO}_{4}{ }^{2-}+\mathrm{PO}_{4}{ }^{3-}$ | $p H=p K_{a_{3}}+\frac{\left[\mathrm{PO}_{4}{ }^{3-}\right]}{\left[H \mathrm{HPO}_{4}{ }^{2-}\right]}$ | Buffer and both exist in third <br> ionization stage |

Note that other polyprotic acids and its salts can be treated in the same maner as $\mathrm{H}_{3} \mathrm{PO}_{4}$.

## Polyprotic Acids And Its Salts

| Example | Solution |
| :---: | :---: |
| Calculate the pH for $0.001 \mathrm{M} \mathrm{Na}_{2} \mathrm{HPO}_{4}$ solution ? | $p H=-\log \sqrt{6.3 X 10^{-8} \cdot 4.2 X 10^{-13}}$ |
| Calculate the pH for $0.1 \mathrm{M} \mathrm{NaHCO}_{3}$ solution ? | $p H=-\log \sqrt{4.4 X 10^{-7} \cdot 4.7 X 10^{-11}}$ |
| Calculate the pH for $0.01 \mathrm{M} \mathrm{NaH}_{2} \mathrm{PO}_{4}$ solution ? | $p H=-\log \sqrt{7.1 X 10^{-3} \cdot 6.3 X 10^{-8}}$ |
| Calculate the pH for $0.1 \mathrm{M} \mathrm{Na}_{2} \mathrm{CO}_{3}$ solution ? | $p O H=-\log \sqrt{\frac{1 X 10^{-14} \cdot \mathrm{O.1}}{4.7 X 1 \mathrm{O}^{-11}}}$ |
| Calculate the pH for $0.1 \mathrm{M} \mathrm{Na}_{3} \mathrm{PO}_{4}$ solution ? | $p O H=-\log \sqrt{\frac{1 X 10^{-14} X . \mathrm{O} .1}{4.2 X 10^{-13}}}$ |

## Summary

In this unit, the concept of the buffer, it's importance in chemistry and in real life and it's types have been investigated. We also discussed the way by which the buffer stabilizes the pH . The calculations of the pH of all sorts of buffer solutions are the main core of this unit. We make sure that the student Knows how to prepare all types of buffer solutions and recognize the role of polyprotic acids in the preparation of buffer solutions .

Exercise 1: Calculate the pH of a solution containing $0.1 \mathrm{M} \mathrm{Na}_{2} \mathrm{CO}_{3}$ and $0.2 \mathrm{M} \mathrm{NaHCO}_{3}$ ? $\mathrm{K}_{\mathrm{a} 2}\left(\mathrm{H}_{2} \mathrm{CO}_{3}\right)=4.7 \mathrm{X10} 0^{-11}$.

Your answer :

## BUFFER SOLUTIONS

Tutorial

Solution 1 :

$$
p H=-\log 4.7 \times 10^{-11}+\log \frac{0.1}{0.2} \approx 10
$$

## Tutorial

Exercise 2 : Calculate the pH of a solution resulting from adding 4 mL of 0.2 M of NaOH solution to 16 mL of a buffer solution containing $0.1 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH}$ $\left(\mathrm{K}_{\mathrm{a}}=1.8 \mathrm{X10}^{-5}\right)$ and $0.2 \mathrm{M} \mathrm{CH}_{3} \mathrm{COONa}$ ?

## Your answer :

## Tutorial

Answer 2: Note that adding NaOH will decrease the number of mmoles of the acid and will increase the number of mmoles of its salt by the same number ( the reaction is $1: 1$ ):

$$
\begin{array}{ccccc}
\mathrm{CH}_{3} \mathrm{COOH} & +\mathrm{NaOH} \rightarrow & \mathrm{CH}_{3} \mathrm{COONa} & +\mathrm{H}_{2} \mathrm{O} & \\
16 \mathrm{X} 0.1=1.6 & 4 \mathrm{X} 0.2=0.8 & 0 & 0 & (\text { mmole })(\mathrm{I}) \\
0.8 & 0 & 0.8 & 0.8 & (\text { mmole })(\mathrm{C})
\end{array}
$$

This means that the number of mmoles of $\mathrm{CH}_{3} \mathrm{COONa}$ will increase by 0.8 mmole to become ( $0.8+16 \mathrm{X} 0.2=4$ mmoles $)$ while the number of mmoles of $\mathrm{CH}_{3} \mathrm{COOH}$ will decrease by 0.8 mmole to become ( $16 \mathrm{X} 0.1-0.8=0.8$ mmole ) . Now we can calculate the pH of the buffer thus :

$$
p H=-\log 1.8 \times 10^{-5}+\log \frac{\overline{16+4(m L)}}{\frac{0.8}{16+4(m L)}}=5.4
$$

## Tutorial

Look at the this video to Buffer Calculations

1. calculate pH of a buffer understand the effect of
2. add HCl , calculate new pH
3. compare with adding HCl to water adding HCl to a buffer solution .

## Tutorial

Exercise 3 : Calculate the pH of a solution resulting from adding 6 mL of 0.2 M HCl to 14 mL of a buffer solution containing $0.2 \mathrm{M} \mathrm{NH}_{3}\left(\mathrm{~K}_{\mathrm{b}}=1.75 \mathrm{X10} 0^{-5}\right)$ and $0.1 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl}$ ?

## Your answer :

## Tutorial

Answer 3 : The added HCl will react with $\mathrm{NH}_{3}$ :

| HCl |  |  |  |
| :---: | :---: | :---: | :---: |
| $6 \mathrm{X} 0.2=1.2$ | + | $\mathrm{NH}_{3}$ | $\rightarrow$ |
| 0 | $\mathrm{NH}_{4} \mathrm{Cl}$ |  |  |
| 0 | 1.6 | 0 |  |

(mmole) (I)
(mmole) (C)

This means that $\mathrm{NH}_{3}$ will decrease by 1.2 mmoles while its salt $\mathrm{NH}_{4} \mathrm{Cl}$ will increase by the same amount i.e 1.2 mmoles, therefore, the pH of the buffer can be calculated thus :

$$
p O H=-\log 1.75 \times 10^{-5}+\log \frac{\frac{[(14 X 0.1)+1.2]}{14+6(\mathrm{ml})}}{\frac{1.6}{14+6(\mathrm{ml})}} \approx 5
$$

$$
\therefore p H=14-5=9
$$

## Tutorial

Exercise 4 : Calculate the change in pH of 250 mL of a buffer solution containing $0.2 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH}$ ( $\mathrm{K}_{\mathrm{a}}=1.8 \mathrm{X10}^{-5}$ ) and $0.2 \mathrm{M} \mathrm{CH}_{3} \mathrm{COONa}$ upon adding 1.0 g of NaOH to it ? This video will help .

Suppose that $0.0200 \mathrm{~mol} \mathrm{NaOH}(\mathrm{s})$ is dissolved in
300 mL of the following buffer solution:
$0.040 \mathrm{M} \mathrm{NaCH}_{3} \mathrm{CO}_{2}(\mathrm{aq})$ and $0.080 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$.
What is the final pH of the solution?
Your answer :

## Tutorial

Just look at this video and realize the difference between adding strong acid or base to a buffer and adding them to just water .

```
Buffer Calculations
```

1. calculate pH of a buffer
2. add HCl , calculate new pH
3. compare with adding HCl to water

## Tutorial

Answer 4 : NaOH will react with $\mathrm{CH}_{3} \mathrm{COOH}$, therefore, the number of mmoles of $\mathrm{CH}_{3} \mathrm{COOH}$ will decrease by $\left[(1.0 \mathrm{~g} / 40) \mathrm{X} 10^{3}=25 \mathrm{mmoles}\right.$ ] to become ( $250 \mathrm{X} 0.2-$ $25=25$ mmoles ) while the number of mmoles of the salt $\mathrm{CH}_{3} \mathrm{COONa}$ will increase by 25 mmoles to become ( $250 \times 0.2+25=75$ mmoles ). Now we can calculate the pH :

$$
p H=-\log 1.8 \times 10^{-5}+\log \frac{\frac{75(\text { mmoles })}{250(\mathrm{~mL})}}{\frac{25(\text { mmoles })}{250(\mathrm{~mL})}} \approx 5.2
$$

## Tutorial

Exercise 5 : Calculate the pH of a solution resulting from adding 20 mL 0.125 M HCl to $25 \mathrm{~mL} 0.12 \mathrm{M} \mathrm{NH}_{3}\left(\mathrm{~K}_{\mathrm{b}}=1.75 \mathrm{X1}^{-5}\right)$ ?

## Your answer :

## BUFFER SOLUTIONS

## Tutorial

Answer 5 :

| HCl | + | $\mathrm{NH}_{3} \rightarrow$ | $\mathrm{NH}_{4} \mathrm{Cl}$ |
| :---: | :---: | :---: | :---: |
| $20 \mathrm{XI} 0.12=3$ | 0 | (mmoles) (I) |  |
| $0.125=2.5$ | 0.5 | 2.5 | (mmoles) (C) |

HCl is the limiting reactant. The remaining $\mathrm{NH}_{3}$ and the produced $\mathrm{NH}_{4} \mathrm{Cl}$ will form a buffer :-

$$
p 0 H=-\log 1.75 \times 10^{-5}+\log \frac{\frac{2.5(\mathrm{mmoles})}{20+25(\mathrm{~mL})}}{\frac{0.5(\mathrm{mmoles})}{20+25(\mathrm{~mL})}} \approx 4.5 \quad \therefore \quad p H=9.5
$$

## Tutorial

Exercise 6 : Calculate the pH of a solution resulting from adding 100 mL 0.04 M HCl to $100 \mathrm{~mL} 0.07 \mathrm{M} \mathrm{NH}_{3}\left(\mathrm{~K}_{\mathrm{b}}=1.75 \mathrm{X10} 0^{-5}\right)$ ?

## Your answer :

## Tutorial

Answer 6 :

$\underset{0}{\mathrm{HCl}}+$| $\mathrm{NH}_{3}$ |
| :---: |
| 3 |$\rightarrow \quad$| $\mathrm{NH}_{4} \mathrm{Cl}$ |
| :---: |
| (mmoles) (C) |

HCl is the limiting reactant. The mixture solution composed of the remaining $\mathrm{NH}_{3}$ and its formed salt $\mathrm{NH}_{4} \mathrm{Cl}$ (buffer solution ) :

$$
p O H=-\log 1.75 \times 10^{-5}+\log \frac{\frac{4}{200(m L)}}{\frac{3}{200(m L)}} \approx 4.9 \quad \therefore \quad p H=9.1
$$

## Tutorial

Exercise 7 : Calculate the pH of a solution resulting from adding 200 mL of 0.05 M NaOH solution to 100 mL of $0.2 \mathrm{M} \mathrm{HA}\left(\mathrm{K}_{\mathrm{a}}=1.75 \times 10^{-5}\right)$ solution ?

## Your answer :

## Tutorial

## Answer 7 :

| HA | $+\mathrm{NaOH} \rightarrow$ | NaA | +NaCl | $+\mathrm{H}_{2} \mathrm{O}$ |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
| 10 | 0 | 10 | 10 | 10 | (mmoles) (C) |

NaOH is the limiting reactant so, the remaining HA and the produced NaA will form a buffer solution :

$$
p H=-\log 1.75 \times 10^{-5}+\log \frac{\frac{10(\text { mmoles })}{300(\mathrm{~mL})}}{\frac{10(\text { mmoles })}{300(\mathrm{~mL})}} \approx 4.8
$$

## Tutorial

Exercise 8: Calculate the pH of a solution resulting from adding 50 mL of 0.1 M NaOH solution to 50 mL of $0.2 \mathrm{M} \mathrm{NH}_{4} \mathrm{Cl}\left[\mathrm{K}_{\mathrm{b}}\left(\mathrm{NH}_{3}\right)=1.75 \mathrm{X} 10^{-5}\right]$ solution ?

Your answer :

## Tutorial

Answer 8 :

$$
\underset{5}{\mathrm{NH}_{4} \mathrm{Cl}}+\underset{0}{\mathrm{NaOH}} \rightarrow \underset{5}{\mathrm{NH}_{3}}+\underset{5}{\mathrm{NaCl}}+\underset{5}{\mathrm{H}_{2} \mathrm{O}}
$$

NaOH is the limiting reactant so , the remaining $\mathrm{NH}_{4} \mathrm{Cl}$ and the produced $\mathrm{NH}_{3}$ will form a buffer solution :

$$
p O H=-\log 1.75 \times 10^{-5}+\log \frac{\frac{5(\text { mmoles })}{100(\mathrm{ml})}}{\frac{5(\mathrm{mmoles})}{100(\mathrm{ml})}} \approx 4.8 \therefore p H=9.2
$$

## Tutorial

Exercise 9 : Calculate the pH of a solution resulting from adding 100 mL of 0.1 M HCl solution to 100 mL of $0.5 \mathrm{M} \mathrm{NaA}\left[\mathrm{K}_{\mathrm{a}}(\mathrm{HA})=1.75 \times 10^{-5}\right]$ solution ?

Your answer :

## Tutorial

## Answer 9 :

$$
\begin{array}{cccc}
\mathrm{NaA} \\
\mathrm{Na} \\
40 & \mathrm{HCl} & \mathrm{HA}+\underset{\mathrm{NaCl}}{\mathrm{Na}}+\underset{(\text { mmoles })(\mathrm{C})}{ }
\end{array}
$$

HCl is the limiting reactant so , the remaining NaA and the produced HA will form a buffer solution :

$$
p H=-\log 1.75 \times 10^{-5}+\log \frac{\frac{40(\text { mmoles })}{200(\mathrm{~mL})}}{\frac{10(\text { mmoles })}{200(\mathrm{~mL})}} \approx 5.4
$$

## Tutorial

Exercise 10 : Calculate the capacity of a buffer solution containing $0.1 \mathrm{M} \mathrm{CH}_{3} \mathrm{COONa}$ and $0.2 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH}\left(\mathrm{pK}_{\mathrm{a}}=4.76\right)$ ?

Your answer :

## Tutorial

$$
\begin{array}{ll}
\text { Answer } 10: & \mathrm{CH}_{3} \mathrm{COOH}
\end{array} \quad \begin{aligned}
& \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}^{+} \\
& \\
& \\
& \\
& \\
& \\
& p H=4.76+\log \frac{0.1}{0.2}=4.5
\end{aligned}
$$

Assume the capacity is x HCl . This means that x moles of HCl will react with x mmoles of $\mathrm{CH}_{3} \mathrm{COONa}$ to form x mmoles of $\mathrm{CH}_{3} \mathrm{COOH}$ thus :

$$
3.5=4.76+\log \frac{(0.1-x)}{(0.2+x)} \therefore x=0.08 \text { moles } H C / L
$$

But if we Assume the capacity is y NaOH . This means that x mmoles of NaOH will react with x mmoles of $\mathrm{CH}_{3} \mathrm{COOH}$ to form x mmoles of $\mathrm{CH}_{3} \mathrm{COONa}$ thus :

$$
5.5=4.76+\log \frac{(0.1+y)}{(0.2-y)} \therefore y=0.15 \text { moles } \mathrm{NaOH} / L
$$

## Tutorial

Exercise 11 : Calculate the pH of a buffer solution that is prepared by adding 25 mL 0.05 M $\mathrm{H}_{2} \mathrm{SO}_{4}$ solution to $50 \mathrm{~mL} 0.1 \mathrm{M} \mathrm{NH}_{3}$ solution ?

Your answer :

## BUFFER SOLUTIONS

## Tutorial

Answer 11 :

$$
\begin{array}{cccl}
\mathrm{H}_{2} \mathrm{SO}_{4} & +2 \mathrm{NH}_{3} & \leftrightarrow\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4} & \\
25 \times 0.05=1.25 & 50 \times 0.1=5 & 0 & \text { (mmoles) (I) } \\
0 & 2.5 & 1.25 & \text { (mmoles) (C) }
\end{array}
$$

$\mathrm{H}_{2} \mathrm{SO}_{4}$ is the limiting reactant so , the remaining $\mathrm{NH}_{3}$ and the produced $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ will form a buffer solution :

$$
p O H=-\log 1.75 \times 10^{-5}+\log \frac{\frac{1.25}{75}}{\frac{2.5}{75}} \approx 4.5 \therefore \quad p H=9.5
$$

## Tutorial

Exercise 12: Which one of the following weak bases would you choose to prepare a buffer solution of $\mathrm{pH}=8$ and why?
$\mathrm{MOH}\left(\mathrm{K}_{\mathrm{b}}=1 \mathrm{X} 10^{-5}\right), \mathrm{NOH}\left(\mathrm{K}_{\mathrm{b}}=1 \mathrm{X} 10^{-8}\right), \mathrm{DOH}\left(\mathrm{K}_{\mathrm{b}}=1 \mathrm{X} 10^{-10}\right)$
Your answer :

## Tutorial

Answer 12: We choose the base that it's $\mathrm{pK}_{\mathrm{b}}$ is the nearest to $(14-8=6)$ in order to prepare a buffer with high capaity i.e. MOH .

على الر اغبين الاستماع الى محاضرات الاستاذ الدكتور/ ابر اهيم زامل الز امل باللغة العربية عن هذا الموضوع الرجوع الىى الروابط التالية :

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