

Analytical chemistry

# Chemical engineering department 

First class / first term
Al-Mustaqbal-college
Lecture Three

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## Lecture Three

## $\Rightarrow \mathrm{pH}$ and pOH

pH scale is a commonly used scale to measure the acidity or the basicity of a substance. The possible values on the pH scale range from 0 to 14 . Acidic substances have pH values ranging from 1 to 7 ( 1 being the most acidic point on the pH scale) and alkaline or basic substances have pH values ranging from 7 to 14 . A perfectly neutral substance would have a pH of exactly 7 .
pH which is an abbreviation of 'potential for hydrogen' or 'power of hydrogen' of a substance can be expressed as the negative logarithm (with base 10) of the hydrogen ion concentration in that substance. Similarly, the pOH of a substance is the negative logarithm of the hydroxide ion concentration in the substance. These quantities can be expressed via the following formulae:

- $\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]$
- $\mathrm{pOH}=-\log [\mathrm{OH}]$


The pH Scale

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## $\Rightarrow$ Relation between $\mathrm{p}\left[\mathrm{H}^{+}\right]$and $\mathrm{p}\left[\mathrm{OH}^{-}\right]$:

pH vs. pOH scale:

|  | pH |  | pOH |
| :---: | :---: | :---: | :---: |
| 1 M sodium hydroxide ( NaOH ) | 14 |  | 0 |
|  | 13 | $\uparrow$ | 1 |
| household ammonia | 12 | $\frac{\square}{n}$ | 2 |
|  | 11 | \% | 3 |
| toothpaste | 10 | ¢ | 4 |
| baking soda solution | 9 |  | 5 |
|  | 8 |  | 6 |
| pure water | 7 |  | 7 |
| urine | 6 |  | 8 |
| black coffee | 5 |  | 9 |
|  | 4 | 는 | 10 |
| cola or vinegar | 3 | ¢ | 11 |
|  | 2 | $\frac{0}{\Sigma}$ | 12 |
| gastric juices | 1 | $\downarrow$ | 13 |
| 1 M hydrochloric acid ( HCl ) | 0 |  | 14 |

Acid solutions usually have protons and basic solutions have hydroxide ions. Concentrations of the ions are low (negative power of ten). pH scale is a convenient way of expressing these low concentrations in simple numbers between 1 and 14.
pH is the negative logarithm to the base ten of hydrogen ion concentration in moles per liter.
$\mathbf{p H}=-\log \left[\mathbf{H}^{+}\right]$
$\mathrm{p}(\mathrm{OH})$ is the negative logarithm to the base ten of hydroxide ion concentration in moles per liter.
$\mathbf{p O H}=-\log \left[\mathrm{OH}^{-}\right]$
In aqueous solutions, $\mathbf{p H}+\mathbf{p}(\mathbf{O H})=14$.
pH scale is based on neutral water, where $[\mathbf{H}+]=[\mathbf{O H}-]=\mathbf{1 0 - 7}$

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For a neutral solution $\mathbf{p H}=-\log [\mathrm{H}+]=-\log [10-7]=+7$
Finding $\mathbf{p}[\mathrm{OH}]=-\log \left[\mathrm{OH}^{-}\right], \quad \mathbf{p H}=\mathbf{1 4} \mathbf{~} \mathbf{p O H}$
Finding $[\mathrm{OH}]$ in bases :
$\mathbf{p H}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]$
1x $10^{-14}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]$

Example $1 \backslash$ A solution of acetic acid $\left(\mathrm{CH}_{3} \mathrm{O}_{2} \mathbf{H}\right)$ has an $\mathbf{H}^{+}$ concentration of $5 \times 10^{-5} \mathrm{M}$. what is the pH of the solution?
Sol. :
$\mathbf{p H}=-\log \left[\mathbf{H}^{+}\right]$
$\mathrm{pH}=-\log \left[5 \times 10^{-5}\right]$
$=4.3$, it is relatively weak acid .

Example $2 \backslash$ find the $\mathbf{p H}$ of a $\mathbf{0 . 0 1 2} \mathbf{M}$ sodium hydroxide ( NaOH ) solution.
Sol. :
$\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]$

$$
=-\log [0.012]=1.92
$$

$\mathrm{pH}+\mathrm{p}(\mathrm{OH})=14$
$\mathrm{pH}=14-1.92=12.08$, the solution has $\mathbf{p H}$ of $\mathbf{1 2 . 0 8}$ and is a strong base.

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pH and pOH are related to one another; THEY ARE NOT INDEPENDENT OF EACH OTHER. As pH increases, pOH decreases. As pH decreases, pOH increases. By knowing what ion you are measuring on which scale, this will tell you whether or not the solution is acidic or basic.

| Ion Concentration | Solution Type | $\mathbf{p H}$ | $\mathbf{p O H}$ |
| :---: | :---: | :---: | :---: |
| $[\mathrm{H}+]>[\mathrm{OH}-]$ | Acidic | $\mathrm{pH}<7$ | $\mathrm{pOH}>7$ |
| $[\mathrm{H}+]<[\mathrm{OH}-]$ | Basic | $\mathrm{pH}>7$ | $\mathrm{pOH}<7$ |
| $[\mathrm{H}+]=[\mathrm{OH}-]$ | Neutral | $\mathrm{pH}=7$ | $\mathrm{pOH}=7$ |

Because these scales are related, an equation can be used to explain their correlation.

$$
\begin{aligned}
& \frac{p H+p O H=14}{p H=14-p O H} \\
& p O H=14-p H
\end{aligned}
$$

*The bottom equations are manipulations of the top equation*
The KEYS to calculations are knowing:

1. Knowing what type of solution you are working with
2. What equation to use first

## Example Calculations:

1. Calculate the pH and pOH of a $0.33 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}$ solution.

- Are you working with an acid or a base?
- Are you given the concentration, or Molarity of that solution?
- Next, plug the concentration or Molarity into the correct equation.

Because this is an acidic solution, we have to calculate pH first.
$p H=-\log [0.33]=$ $\qquad$

Now we can calculate the pOH , because we have calculated the pH . $p O H=14-p H=$ $\qquad$ $=$ $\qquad$
2. Calculate the pH and pOH of a 0.25 M NaOH solution.

- Are you working with an acid or a base? $\qquad$
- Are you given the concentration, or Molarity of that solution?
- Next, plug the concentration or Molarity into the correct equation.

Because this is a basic solution, we have to calculate pOH first.

$$
p O H=-\log [0.25]=
$$

$\qquad$
Now we can calculate the pH , because we have calculated the pOH .
$p H=14-p O H=$ $\qquad$ = $\qquad$

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Ex/ What is the pH of a 0.0005 M solution of NaOH at $25^{\circ} \mathrm{C}$ ?
Solution / $\quad \mathrm{NaOH} \rightarrow \mathrm{Na}^{+}+\mathrm{OH}^{-}$

$$
\begin{aligned}
{\left[\mathrm{OH}^{=}\right] } & =0.0005 \mathrm{M}=5 \times 10^{-4} \mathrm{M} \\
\mathrm{pOH} & =-\log \left[\mathrm{OH}^{-}\right] \\
& =-\log 5 \times 10^{-4} \\
& =-\log 5+4 \log 10 \\
& =-0.699+4 \\
& =3.301 \\
\mathrm{pH}= & 14-3.401=10.7
\end{aligned}
$$

$\mathrm{Ex} /$ What is the pH of a $0.1 \mathrm{M} \mathrm{NH}_{3}$ solution ? $\mathrm{K}_{\mathrm{b}} 1.8 \times 10^{-5}$
Solution /
$\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{NH}_{4}^{+}+\mathrm{OH}^{-}$
0.1

0
0
0.1-X X X

$$
\begin{aligned}
& \mathrm{K}_{\mathrm{b}}=\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right] /\left[\mathrm{NH}_{3}\right] \\
& 1.8 \times 10^{-5}=(\mathrm{X})(\mathrm{X}) / 0.1-\mathrm{X} \\
& 1.8 \times 10^{-5}=\mathrm{X}^{2} / 0.1 \\
& \mathrm{X}^{2}=1.8 \times 10^{-6} \\
& \mathrm{X}=1.34 \times 10^{-3}=\left[\mathrm{OH}^{-}\right]
\end{aligned}
$$

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$$
\begin{aligned}
\mathrm{pOH}= & -\log \left[\mathrm{OH}^{-}\right]=-\log 1.34 \times 10^{-3}=2.87 \\
& \mathrm{pOH}+\mathrm{pH}=14 \\
& \mathrm{pH} 14-2.87=11.12
\end{aligned}
$$

## $\Rightarrow$ Buffer Solution

A buffer solution is an aqueous solution consisting of a mixture of a weak acid and its conjugate base, or vice versa. Its pH changes very little when a small amount of strong acid or base is added to it. Buffer solutions are used as a means of keeping pH at a nearly constant value in' a wide variety of chemical applications. In nature, there are many systems that use buffering for pH regulation. For example, the bicarbonate buffering system is used to regulate the pH of blood.

## Types:

1- Acidic Buffer $(\mathrm{pH}<7) \quad$ weak acid $\quad+\quad$ its sodium or potassium salt

> ethanoic acid sodium ethanoate

2- Alkaline Buffer ( $\mathrm{pH}>7$ ) weak base + its chloride Ammonia ammonium chloride

## 1- Acidic buffer solutions

An acidic buffer solution is one which has a pH less than 7, and commonly made from a weak acid and one of its salts often a sodium salt. A common example would be a mixture of ethanoic acid and sodium ethanoate in solution. In this case, if the solution contained equal molar concentrations of

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both the acid and it salt, it would have a pH of 4,76 . It wouldn't matter what the concentrations were, as long as ethanoate in solution. they were the same.

It 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.
Ethanoic acid is a weak acid, and the position of this equilibrium will be to the left:
$\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})} \leftrightarrow \mathrm{H}^{+}{ }_{(\mathrm{aq})}+\mathrm{CH}^{-} \mathrm{COO}^{-}{ }_{(\mathrm{aq})}$
Adding sodium ethanoate to this adds lots of extra ethanoate ions. According to Le Chatelier's Principle, that will tip the position of the equilibrium even future to the left. the solution will Therefore contain these Important things:

- Lots of un-ionized ethanoic acid.
- Lots of ethanoate ions from sodium ethanoate.
- Enough hydrogen ions to make the solution acidic.


## 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 ethanoate ions to make ethanoic acid. Although the reaction is reversible, since ethanoic acid is a weak acid, most of the new hydrogen ions are removed in this way so the pH won't change very much but because of the equilibrium involved, it will fall a little bit.

$$
\mathrm{CH}_{3} \mathrm{COO}_{(\mathrm{aq})}^{-}+\mathrm{H}^{+} \leftrightarrow \mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})}
$$

## Adding an alkali to this buffer solution

Alkaline solutions contain hydroxide ions and the buffer solution removes most of these. This time the situation is a bit more complicated because there are two processes which can remove hydroxide ions.

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- Removal by reacting with ethanoic acid

The most likely acidic substance which a hydroxide ion is going to collide with is an ethanoic acid molecule. They will react to form ethanoate ions and water.

$$
\mathrm{CH} 3 \mathrm{COOH}_{(\mathrm{aq})}+\mathrm{OH}_{(\mathrm{aq})}^{-} \leftrightarrow \mathrm{CH}_{3} \mathrm{COO}_{(\mathrm{aq})}^{-}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{L})}
$$

Because most of the new hydroxide ions are removed, the pH doesn't increase very much.

- Removal of the hydroxide ions by reacting with hydrogen ions

Remember that there are some hydrogen ions present from the ionization of the ethanoic acid.
$\mathrm{CH}_{3} \mathrm{COOH}_{(\mathrm{aq})} \leftrightarrow \mathrm{CH}_{3} \mathrm{COO}_{(\mathrm{aq})}^{-}+\mathrm{H}_{(\mathrm{aq})}^{+}$
Hydroxide ions can combine with these to make water. As soon as this happens, the equilibrium tips to replace them. This keeps on happening until most of the hydroxide ions are removed.

Equilibrium moves to replace the removed hydrogen lons.

## $\mathrm{CH}_{3} \mathrm{COOH}_{(\text {(aq })} \leftrightarrow \mathrm{CH}_{3} \mathrm{COO}^{-}{ }_{(\mathrm{aq})}+\mathrm{H}^{+}{ }_{(\mathrm{aq})}$

Hydroxide lons combine with these to make water

Again, because you have equilibria involved, not all of the hydroxide ions are removed just most of them. The water formed re-ionizes to a very small extent to give a few hydrogen ions and hydroxide ions.

