## pH

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## What is an Acid?

* An acid is a substance which, when dissolved in water, releases protons.
* The extent of dissociation, that is, the amount of protons released compared to the total amount of compound, is a measure of the strength of the acid.
* For example, HCl (hydrochloric acid) is a strong acid, because it dissociates completely in water, generating free $\left[\mathrm{H}^{+}\right]$and $\left[\mathrm{Cl}^{-}\right]$.


## Pure Water is Neutral

Pure water contains small, but equal amounts of ions: $\mathrm{H}_{3} \mathrm{O}^{+}$and $\mathrm{OH}^{-}$
$\mathrm{H}_{2} \mathrm{O}+\mathrm{H}_{2} \mathrm{O}$

hydronium hydroxide ion ion
$1 \times 10^{-7} \mathrm{M} \quad 1 \times 10^{-7} \mathrm{M}$

## Ion Product of Water $\mathrm{K}_{\mathrm{w}}$

$$
\begin{aligned}
{[\quad]=} & \text { Molar concentration } \\
\mathrm{K}_{\mathrm{w}}= & {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right] } \\
& =\left[1 \times 10^{-7}\right]\left[1 \times 10^{-7}\right] \\
& =1 \times 10^{-14}
\end{aligned}
$$

## Acids

Olncrease $\mathrm{H}^{+}$
$\mathrm{HCl}(\mathrm{g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \quad \longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})$
More $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right.$] than water $>1 \times 10^{-7} \mathrm{M}$

- As $\mathrm{H}_{3} \mathrm{O}^{+}$increases, $\mathrm{OH}^{-}$decreases

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]>\left[\mathrm{OH}^{-}\right]
$$



## What is the pH scale？

Acidic
$\left[\mathrm{H}^{+}\right]$

## ＊The pH scale measures how

 acidic or basic a solution is．| pH |  |
| :---: | :---: |
| 0 |  |
| 0.1 M hydrochloric a |  |
|  |  |
|  |  |
|  |  |
| 4 | 4．2 beer |
| $5 \text { 二 } \begin{aligned} & 4.6 \text { acir rain } \\ & 5.0 \text { cheese } \end{aligned}$ |  |
| 6 － 6.0 yogurt |  |
|  |  |
|  |  |
| $8-8.0$ seawater |  |
| 8.4 sodium |  |
| 10 |  |
|  |  |
| 11 － 10.5 milk of magnesia |  |
| 12 |  |
| － 12.4 limewater |  |
| 13 － 13.2 oven cleaner |  |
|  | M potassium hy |

## Importance of pH in environmental engineering

In environmental engineering pH must be considered in:

* Chemical coagulation
* Disinfection
* Water softening
* Corrosion control
* Microorganisms in biological treatment
* Sludge dewatering
* Oxidation of certain substances (such as cyanide)


## Precipitation of Metals from Wastewater

The Solubility of Metals is Dependent on pH


## Hydroxide Precipitation

Minimum Solubility (Best Removal) Value for Some Metals

Cadmium pH 11.0<br>Copper pH 8.1<br>Chromium<br>pH 7.5<br>Nickel<br>pH 10.8<br>Zinc<br>pH 10.1

## Dissociation Constants

* For a generalized acid dissociation,
$\mathrm{HA}(a q)+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{A}^{-}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q)$
the equilibrium expression is

$$
K_{c}=K_{a}=\frac{\left[H_{3} O^{+}\right]\left[A^{-}\right]}{[H A]}
$$

* This equilibrium constant is called the acid-dissociation constant, $K_{a}$.
* $\mathrm{pH}=-\log \left\{\mathrm{H}^{+}\right\}$
* pH range o-14
* pH 7 @ $25^{\circ} \mathrm{C}$ represent absolute neutrality
* Neutrality @ $0^{\circ} \mathrm{C} \rightarrow \mathrm{pH} 7.5$
* Neutrality @ $60^{\circ} \mathrm{C} \rightarrow \mathrm{pH} 6.5$
* $\mathrm{K}_{\mathrm{w}}$ changes with change in temperature $\rightarrow \mathrm{pH}$ of neutrality changes with temperature


## Interpretation of pH Data

* pH data should be interpreted in terms of hydrogen ion activity
* Approximately we can assume

$$
\left[\mathrm{H}^{+}\right]=\left\{\mathrm{H}^{+}\right\}
$$

$\mathrm{pH}+\mathrm{pOH}=14$
[ $\mathrm{H}^{+}$] and $\left[\mathrm{OH}^{-}\right]$can never be zero

## Activity and Concentration

Until now we have assumed that activity, $a$, is equal to concentration, $c$, by setting $\gamma=1$ when dealing with dilute aqueous solutions...

* Activity - "effective concentration"
* Ion-ion and ion- $\mathrm{H}_{2} \mathrm{O}$ interactions (hydration shell) cause number of ions available to react chemically ("free" ions) to be less than the number present
* Concentration can be related to activity using the activity coefficient $\gamma$, where [a] = $\gamma$ (c)


## But ions don't behave ideally . . .

Concentration related to activity using the activity coefficient $\gamma$, where $\quad[a]=\gamma(c)$

* The value of $\gamma$ depends on:
* Concentration of ions and charge in the solution
* Charge of the ion
* Diameter of the ion
* Ionic strength, $I=$ concentration of ions and charge in solution

$$
I=1 / 2 \sum m_{\mathrm{i}} \mathrm{z}_{\mathrm{i}}^{2}
$$

* where $m_{i}=$ concentration of each ion in moles per $L$, $z_{i}=$ charge of ion
* Activity coefficient $\gamma_{z} \rightarrow 1$ as concentrations $\rightarrow 0$ and tend to be <1 except for brines


## Interpretation of pH Data

* pH does not measure total acidity.
* Compare the pH of 0.1N Sulfuric acid and acetic acid
* They have the same neutralizing value



## Testing the pH of Solutions

The pH of solutions can be determined using

* a pH meter
* pH paper
* indicators that have specific colors at different pH values



## How Do We Measure pH?

|  | pH range for color change |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 0 | 2 | , |  | 68 | $8 \quad 10$ | 0 | 12 | 14 |
| Methyl violet | Yellow |  | Viol |  |  |  |  |  |  |  |
| Thymol blue |  | Red |  | Yellow |  | Yellow | Bl | Slue |  |  |
| Methyl orange |  |  |  | d | Yellow |  |  |  |  |  |
| Methyl red |  |  |  | Red |  | Yellow |  |  |  |  |
| Bromthymol blue |  |  |  |  | Yellow | Bl | lue |  |  |  |
| Phenolphthalein |  |  |  |  |  | Colorless |  | Pink |  |  |
| Alizarin yellow R |  |  |  |  |  |  | Yellow |  |  | d |

* Litmus paper
* "Red" paper turns blue above $\sim \mathrm{pH}=8$
* "Blue" paper turns red below $\sim \mathrm{pH}=5$
* An indicator
* Compound that changes color in solution.

