

## Acids and Bases

Chapter 15

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## Acids

Have a sour taste. Vinegar owes its taste to acetic acid. Citrus fruits contain citric acid.
React with certain metals to produce hydrogen gas.
React with carbonates and bicarbonates to produce carbon dioxide gas

## Bases

Have a bitter taste.
Feel slippery. Many soaps contain bases.


What is the concentration of $\mathrm{OH}^{-}$ions in a HCl solution whose hydrogen ion concentration is 1.3 M ?

$$
\begin{gathered}
K_{w}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14} \\
{\left[\mathrm{H}^{+}\right]=1.3 \mathrm{M}} \\
{\left[\mathrm{OH}^{-}\right]=\frac{K_{w}}{\left[\mathrm{H}^{+}\right]}=\frac{1 \times 10^{-14}}{1.3}=7.7 \times 10^{-15} \mathrm{M}}
\end{gathered}
$$

At $25^{\circ} \mathrm{C}$
$K_{w}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}$

Solution Is
$\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right]$
$\left[\mathrm{H}^{+}\right]>\left[\mathrm{OH}^{-}\right]$
$\left[\mathrm{H}^{+}\right]<\left[\mathrm{OH}^{-}\right]$
neutral
acidic
basic


The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. What is the $\mathrm{H}^{+}$ion concentration of the rainwater?

$$
\begin{aligned}
\mathrm{pH} & =-\log \left[\mathrm{H}^{+}\right] \\
{\left[\mathrm{H}^{+}\right]=10^{-\mathrm{pH}} } & =10^{-4.82}=1.5 \times 10^{-5} \mathrm{M}
\end{aligned}
$$

The $\mathrm{OH}^{-}$ion concentration of a blood sample is $2.5 \times 10^{-7} \mathrm{M}$. What is the pH of the blood?

$$
\begin{gathered}
\mathrm{pH}+\mathrm{pOH}=14.00 \\
\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]=-\log \left(2.5 \times 10^{-7}\right)=6.60 \\
\mathrm{pH}=14.00-\mathrm{pOH}=14.00-6.60=7.40
\end{gathered}
$$

## Weak Acids are weak electrolytes

$\mathrm{HF}(a q)+\mathrm{H}_{2} \mathrm{O}(\mathrm{n}) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{F}^{-}(a q)$
$\mathrm{HNO}_{2}(a q)+\mathrm{H}_{2} \mathrm{O}(\rho) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{NO}_{2}^{-}(a q)$
$\mathrm{HSO}_{4}{ }^{-}(a q)+\mathrm{H}_{2} \mathrm{O}(\Lambda) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{SO}_{4}{ }^{2-}(a q)$
$\mathrm{H}_{2} \mathrm{O}_{( }()+\mathrm{H}_{2} \mathrm{O}(\Omega) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{OH}^{-}(a q)$

## Strong Bases are strong electrolytes

$$
\begin{aligned}
& \mathrm{NaOH}(s) \xrightarrow{\mathrm{H}_{2} \mathrm{O}} \mathrm{Na}^{+}(a q)+\mathrm{OH}^{-}(a q) \\
& \mathrm{KOH}(s) \xrightarrow{\mathrm{H}_{2} \mathrm{O}} \mathrm{~K}^{+}(a q)+\mathrm{OH}^{-}(a q) \\
& \mathrm{Ba}(\mathrm{OH})_{2}(s) \xrightarrow{\mathrm{H}_{2} \mathrm{O}} \mathrm{Ba}^{2+}(a q)+2 \mathrm{OH}^{-}(a q)
\end{aligned}
$$




| Nome of Acid | Formula | Strusture | $\kappa$. | Conjugate tree | $\mathrm{K}_{4}{ }^{\text {a }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| H2derituas ixi- | ${ }^{\text {H1}}$ | 11 F | 71 $\times 13$ - | 1 | $1.4 \times 10^{11}$ |
|  | -1.nve, | $\mathrm{O}-\mathrm{N}=0-\mathrm{F}$ | 13) 130 | NO. | 2/19" |
| Anstykalise in: axil usqcin: | c,11\% |  | $9 \mathrm{C} \times 1 \mathrm{a}^{-}$ | 1, 114 |  |
| Fersice cis | Hixum |  | $1.7 \times 1 \mathrm{~m}^{-}$ | HCOOS | s. $\times \times 10^{11}$ |
| Naxrse siis" | c.110.e | H-6, | sto 13 | 1-110.4 | W/ / $1^{\prime \prime}$ |
| R.amie wek | C. H COONH |  | $43 / 13^{*}$ | C. $\mathrm{H}, \mathrm{CO}$ | $1.5710^{\circ}$ |
| Awrivenil | ctrom |  | $18 \times 13^{-}$ | rimeor | is $\times 1{ }^{\text {ar }}$ |
|  |  | H | $40 \times 11^{12}$ |  | $2.3 \times 10^{\prime}$ |
| (tyas) | c.llow |  | 13) $13^{\text {² }}$ | 1,110\% | $3 \times 1$ |



Weak Acids (HA) and Acid Ionization Constants

$$
\begin{aligned}
\mathrm{HA}(a q)+\mathrm{H}_{2} \mathrm{O}(\eta & \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{A}^{-}(a q) \\
\mathrm{HA}(a q) & \rightleftarrows \mathrm{H}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq}) \\
K_{a} & =\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}
\end{aligned}
$$

$K_{a}$ is the acid ionization constant

$$
\left.K_{a} \uparrow \quad \begin{gathered}
\text { weak acid } \\
\text { strength }
\end{gathered} \right\rvert\,
$$

## What is the pH of a 0.5 MHF solution (at $25^{\circ} \mathrm{C}$ )?

| $\mathrm{HF}(a q)$ | $\longrightarrow \mathrm{H}^{+}(a q)+\mathrm{F}$ | aq) $K_{a}=\frac{\left[\mathrm{H}^{+}\right.}{[H}$ | $]=7.1 \times 10^{-4}$ |
| :---: | :---: | :---: | :---: |
|  | $\mathrm{HF}(\mathrm{aq}) \rightleftarrows \mathrm{H}^{+}(a q)+\mathrm{F}^{-}(\mathrm{aq})$ |  |  |
| Initial (M) | 0.50 | $0.00 \quad 0.00$ |  |
| Change ( $M$ ) | -x | +x +x |  |
| Equilibrium ( $M$ ) | $0.50-x$ | $x \quad x$ |  |
| $K=\frac{x^{2}}{0.50-x}$ | $7.1 \times 10^{-4}$ | $K_{a} \ll 1 \quad 0.50-x \approx 0.50$ |  |
| $K_{a} \approx \frac{x^{2}}{0.50}=7.1 \times 10^{-4}$ |  | $x^{2}=3.55 \times 10^{-4}$ | $x=0.019 \mathrm{M}$ |
| $\left[\mathrm{H}^{+}\right]=\left[\mathrm{F}^{-}\right]=0.019 \mathrm{M}$ |  | $\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=1.72$ |  |
| $[\mathrm{HF}]=0.50-x=0.48 \mathrm{M}$ |  | 18 |  |

When can I use the approximation?

$$
K_{a} \ll 1 \quad 0.50-x \approx 0.50
$$

When $x$ is less than $5 \%$ of the value from which it is subtracted.

$$
x=0.019 \quad \frac{0.019 M}{0.50 M} \times 100 \%=3.8 \% \quad \begin{gathered}
\text { Less than } 5 \% \\
\text { Approximation ok. }
\end{gathered}
$$

What is the pH of a 0.05 MHF solution (at $25^{\circ} \mathrm{C}$ )?

| $K_{a} \approx \frac{x^{2}}{0.05}=7.1 \times 10^{-4}$ | $x=0.006 \mathrm{M}$ |
| :---: | :---: |
| $\frac{0.006 \mathrm{M}}{0.05 \mathrm{M}} \times 100 \%=12 \%$ | More than $5 \%$ |
| Approximation not ok. |  |

Must solve for $x$ exactly using quadratic equation or method of successive approximations.

## Solving weak acid ionization problems:

1. Identify the major species that can affect the pH .

- In most cases, you can ignore the autoionization of water.
- Ignore $\left[\mathrm{OH}^{-}\right]$because it is determined by $\left[\mathrm{H}^{+}\right]$.

2. Use ICE to express the equilibrium concentrations in terms of single unknown $x$.
3. Write $K_{a}$ in terms of equilibrium concentrations. Solve for $x$ by the approximation method. If approximation is not valid, solve for $x$ exactly.
4. Calculate concentrations of all species and/or pH of the solution.

## What is the pH of a 0.122 M monoprotic acid whose <br> $K_{a}$ is $5.7 \times 10^{-4}$ ?

|  | $\mathrm{HA}(a q) \rightleftarrows$ | $\mathrm{H}^{+}(a q)+\mathrm{A}^{-}(a q)$ |  |
| :--- | :---: | :---: | :---: |
| Initial $(M)$ | 0.122 | 0.00 | 0.00 |
| Change $(M)$ | $-x$ | $+x$ | $+x$ |
| Equilibrium $(M)$ | $0.122-x$ | $x$ | $x$ |

$$
K_{a}=\frac{x^{2}}{0.122-x}=5.7 \times 10^{-4} \quad K_{a} \ll 1 \quad 0.122-x \approx 0.122
$$

$$
K_{a} \approx \frac{x^{2}}{0.122}=5.7 \times 10^{-4} \quad x^{2}=6.95 \times 10^{-5} \quad x=0.0083 \mathrm{M}
$$

$$
\frac{0.0083 M}{0.122 M} \times 100 \%=6.8 \% \quad \text { More than } 5 \%
$$

For a monoprotic acid HA
Percent ionization $=\frac{\left[\mathrm{H}^{+}\right]}{[\mathrm{HA}]_{0}} \times 100 \% \quad[\mathrm{HA}]_{0}=$ initial concentration


Weak Bases and Base Ionization Constants

$$
\mathrm{NH}_{3}(a q)+\mathrm{H}_{2} \mathrm{O}\left(\rho \rightleftarrows \mathrm{NH}_{4}^{+}(a q)+\mathrm{OH}^{-}(a q)\right.
$$

$$
K_{b}=\frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{3}\right]}
$$

$K_{b}$ is the base ionization constant

$$
K_{b} \uparrow \quad \begin{gathered}
\text { weak base } \\
\text { strength }
\end{gathered}
$$

Solve weak base problems like weak acids except solve for $[\mathrm{OH}-]$ instead of $\left[\mathrm{H}^{+}\right]$.

| Nurnm af Bxam | Fismuln | Strextum | $K_{3}{ }^{\prime}$ | Conjugate <br> Anaik | $\kappa_{1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Luty alim $^{\text {a }}$ |  | C3－tH2－N－1 | － $6 \times 118$－ | ¢15\％． | 1s×1 |
| Statra ins | CH $\times$ \％． | cr． CH | $+6 \times 1 \mathrm{in}^{-1}$ | crint． | $23 / 16^{-1}$ |
| smaves． | $\mathrm{NH}_{1}$ | H－N－M | $13<w^{\prime}$ | su！ | $x \backslash \mathrm{v}^{\text { }}$ |
| Pexas： | ぐロッ |  | 1：2w | Cusim | 3010 |
| ～．．${ }^{\text {．．}}$ | $\cdots$ |  | ＂$\times \ldots$ | 二， | co |
| Culieces | Lu，¢ $\times 1$ | o | $\because 3 \times 10^{\prime \prime}$ | çu Ṅ¢ | 4．4 |
| Hina | （N1290） | $\circ$ |  | nexome | nfi |
|  |  |  |  |  |  |

## Diprotic and Triprotic Acids

－May yield more than one hydrogen ion per molecule．
－Ionize in a stepwise manner；that is，they lose one proton at a time．
－An ionization constant expression can be written for each ionization stage．
－Consequently，two or more equilibrium constant expressions must often be used to calculate the concentrations of species in the acid solution．


Ionization Constants of Conjugate Acid－Base Pairs

$$
\begin{array}{cl}
\mathrm{HA}(a q) \rightleftarrows \mathrm{H}^{+}(a q)+\not A^{(a q)} & K_{a} \\
\frac{A^{-}(a q)+\mathrm{H}_{2} \mathrm{O}\left(\eta \rightleftarrows \mathrm{OH}^{-}(a q)+\mathrm{HA}^{(a q)}\right.}{\mathrm{H}_{2} \mathrm{O}\left(\eta \rightleftharpoons \mathrm{H}^{+}(a q)+\mathrm{OH}^{-}(a q)\right.} & K_{b} \\
K_{w}
\end{array}
$$

$$
K_{a} K_{b}=K_{w}
$$

Weak Acid and Its Conjugate Base

$$
K_{a}=\frac{K_{w}}{K_{b}} \quad K_{b}=\frac{K_{w}}{K_{a}}
$$



Molecular Structure and Acid Strength

$\mathrm{HF} \ll \mathrm{HCl}<\mathrm{HBr}<\mathrm{HI}$


Molecular Structure and Oxoacid Strength


The O-H bond will be more polar and easier to break if:

- $Z$ is very electronegative or
- $Z$ is in a high oxidation state


Molecular Structure and Acid Strength
2. Oxoacids having the same central atom ( $Z$ ) but different numbers of attached groups.

Acid strength increases as the oxidation number of $Z$ increases.


## Acid-Base Properties of Salts

## Acid Solutions:

Salts derived from a strong acid and a weak base.

$$
\begin{aligned}
& \mathrm{NH}_{4} \mathrm{Cl}(s) \stackrel{\mathrm{H}_{2} \mathrm{O}}{\rightleftarrows} \mathrm{NH}_{4}^{+}(a q)+\mathrm{Cl}^{-}(a q) \\
& \mathrm{NH}_{4}^{+}(a q) \rightleftarrows \mathrm{NH}_{3}(a q)+\mathrm{H}^{+}(a q)
\end{aligned}
$$

Salts with small, highly charged metal cations (e.g. $\mathrm{Al}^{3+}$, $\mathrm{Cr}^{3+}$, and $\mathrm{Be}^{2+}$ ) and the conjugate base of a strong acid.

$$
\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}^{3+}(a q) \rightleftarrows \mathrm{Al}(\mathrm{OH})\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}^{2+}(a q)+\mathrm{H}^{+}(a q)
$$

## Acid-Base Properties of Salts

## Solutions in which both the cation and the anion hydrolyze:

- $K_{b}$ for the anion $>K_{a}$ for the cation, solution will be basic
- $K_{b}$ for the anion $<K_{a}$ for the cation, solution will be acidic
- $K_{b}$ for the anion $\approx K_{a}$ for the cation, solution will be neutral


$$
\begin{aligned}
& \mathrm{Na}_{2} \mathrm{O}(s)+\mathrm{H}_{2} \mathrm{O}(\Lambda \longrightarrow 2 \mathrm{NaOH}(a q) \\
& \mathrm{CO}_{2}(g)+\mathrm{H}_{2} \mathrm{O}\left(\Lambda \rightleftarrows \mathrm{H}_{2} \mathrm{CO}_{3}(a q)\right. \\
& \mathrm{N}_{2} \mathrm{O}_{5}(g)+\mathrm{H}_{2} \mathrm{O}\left(\Lambda \rightleftarrows 2 \mathrm{HNO}_{3}(a q)\right.
\end{aligned}
$$



## Definition of An Acid

Arrhenius acid is a substance that produces $\mathrm{H}^{+}\left(\mathrm{H}_{3} \mathrm{O}^{+}\right)$in water
A Bronsted acid is a proton donor
A Lewis acid is a substance that can accept a pair of electrons
A Lewis base is a substance that can donate a pair of electrons


acid base


