## Acid-Base Equilibria

## Chapter 16

## Chemistry, The Central Science 11th edition



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## Acids and Bases

- Acids and bases are found in many common substances and are important in life processes.
- A range of chemical processes from industrial to biological ones, from reactions in the lab to those occurring in the environment, involve either an acid or a base.
- As such, a massive amount of chemistry can be understood in terms of acid-base reactions.
- There are several models for what constitutes an acid or a base - three models to be discussed in this chapter.


## Acids and Bases

| Acid | Base |
| :--- | :--- |
| Tastes sour | Tastes bitter |
| Stings skin | Feels slippery |
| Turns litmus red | Turns litmus blue |
| Turns phenolphthalein <br> colourless | Turns phenolphthalein pink |
| Corrosive to metals | Fouling on metal surfaces |
| Examples: <br> - Ascorbic acid (vitamin C) <br> - Citric acid ( lemon and <br> orange) | Examples: <br> $-\mathrm{CaCO}_{3}$ is used in antacid <br> tables <br> -NaOH to unblock drains |

## Acids and Bases

- React together to form a salt with loss of the characteristic acid/base properties.


## Arrhenius Theory

- Acid: substance that produces $\mathrm{H}^{+}$in aqueous solution
- Base: substance that produces $\mathrm{OH}^{-}$in aqueous solution


## Acids and Bases

Examples of Arrhenius acids and bases:
Acid $\quad \mathrm{HCl}(\mathrm{g}) \xrightarrow{\mathrm{H}_{2} \mathrm{O}} \mathrm{H}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})$
Base $\quad \mathrm{NaOH}(\mathrm{g}) \xrightarrow{\mathrm{H}_{2} \mathrm{O}} \mathrm{Na}^{+}(\mathrm{ag})+\mathrm{OH}^{-}(\mathrm{aq})$
$\mathrm{HCl}+\mathrm{NaOH} \rightarrow \mathrm{Na}^{+}+\mathrm{Cl}^{-}+\mathrm{H}_{2} \mathrm{O}$
acid + base $\rightarrow$ salt + water.
$\Rightarrow$ The Arrhenius concept is limited to substances that dissolve in water.

## Brønsted-Lowry Acids and Bases

In 1923 two chemists, Brønsted and Lowry suggested a more general definition of acids and bases.
-Their concept was based on the fact that acid-base reactions to involve the transfer of a proton, (a proton is an $\mathrm{H}^{+}$ion), from an acid to a base.
-This transfer may or may not involve water.

- An acid is a species that $\qquad$ a proton.
- A base is a species that $\qquad$ a proton.


## Brønsted-Lowry Acids and Bases

## Examples

- Acids:
$\mathrm{HCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})$
$\mathrm{NH}_{4}{ }^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{NH}_{3}(\mathrm{aq})$
- Bases:
$\mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{OH}^{-}(\mathrm{aq})+\mathrm{NH}_{4}{ }^{+}(\mathrm{aq})$ $\mathrm{CO}_{3}{ }^{2-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{OH}^{-}(\mathrm{aq})+\mathrm{HCO}_{3}^{-}(\mathrm{aq})$


## Brønsted-Lowry Acids and Bases

## The $\mathrm{H}^{+}$Ion in Water

- If acid-base reactions are proton ( $\mathrm{H}^{+}$ion) transfer reactions, we need to know what the $\mathrm{H}^{+}$ion is.
- The hydrogen ion, $\mathrm{H}^{+}$ion , is a very small "bare" proton with no surrounding valence electron.
- This small, positively charged particle interacts with the nonbonding electron pairs (lone pair) of $\mathrm{H}_{2} \mathrm{O}$ molecules to form a hydronium ion, $\mathrm{H}_{3} \underline{\mathrm{O}^{+}}$.


## Brønsted-Lowry Acids and Bases

## The $\mathrm{H}^{+}$Ion in Water



The hydronium ion

- $\mathrm{H}^{+}$and $\mathrm{H}_{3} \mathrm{O}^{+}$represent the same thing - hydrated proton.
- The can be used interchangeably.


## Brønsted-Lowry Acids and Bases

## Proton-Transfer Reactions

Let us see what happens when an acid dissolves in water...
Consider: $\mathrm{HCl}(\mathrm{g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})$


The polar $\mathrm{H}_{2} \mathrm{O}$ molecule promotes the ionization of acids in an aqueous (water) solution by accepting a proton to form $\mathrm{H}_{3} \mathrm{O}^{+}$.

## Brønsted-Lowry Acids and Bases

## Proton-Transfer Reactions

Brønsted and Lowry proposed that acids and bases should be defined as follows:

ACID : An acid is a substance (molecule or ion) that can transfer a proton to another substance.

BASE : A base is a substance that can accept a proton from another substance.

These are termed Brønsted-Lowry acids and bases.

## Brønsted-Lowry Acids and Bases

## Proton-Transfer Reactions

- Simply put, according to the Brønsted-Lowry definitions:

An acid is a proton donor A base is a proton acceptor

- The Brønsted-Lowry concept is on proton transfer and also applies to reactions that do not occur in aqueous solution.

- This reaction occurs in the gas phase


## Brønsted-Lowry Acids and Bases

## Proton-Transfer Reactions

Amphiprotic substances

- Consider the reaction of $\mathrm{H}_{2} \mathrm{O}$ with HCl in [1] and $\mathrm{NH}_{3}$ in [2].

- In [1] $\mathrm{H}_{2} \mathrm{O}$ is a Bronsted-Lowry base it $\qquad$ a proton.
- In [2] $\mathrm{H}_{2} \mathrm{O}$ is a Bronsted-Lowry acid it $\qquad$ a proton.


## Brønsted-Lowry Acids and Bases

## Proton-Transfer Reactions

A substance that is capable of acting as either an acid or a base is called amphiprotic.

## Brønsted-Lowry Acids and Bases

## Conjugate Acid-Base Pairs

- From the Latin word conjugare, meaning "to join together."
- Reactions between acids and bases always yield their conjugate bases and acids.



## Brønsted-Lowry Acids and Bases

## Conjugate Acid-Base Pairs

- Consider the reaction of an acid (HA) with water:

$$
\mathrm{HA}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{A}^{-}(a q)
$$

- After HA (acid) loses its proton it is converted into $A^{-}$ (base). Therefore HA and $\mathrm{A}^{-}$are conjugate acid-base pairs.
- After $\mathrm{H}_{2} \mathrm{O}$ (base) gains a proton it is converted into $\mathrm{H}_{3} \mathrm{O}^{+}$ (acid). Therefore, $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{H}_{3} \mathrm{O}^{+}$are conjugate acid-base pairs.
- Conjugate acid-base pairs differ by only one proton.


## Brønsted-Lowry Acids and Bases

## Conjugate Acid-Base Pairs



## Brønsted-Lowry Acids and Bases

## Conjugate Acid-Base Pairs

## Examples

## conjugate acid

$$
\begin{aligned}
& \mathrm{H}_{3} \mathrm{O}^{+} \\
& \mathrm{NH}_{4}^{+} \\
& \mathrm{H}_{2} \mathrm{CO}_{3} \\
& \mathrm{H}_{2} \mathrm{PO}_{4}{ }^{2-}
\end{aligned}
$$

conjugate base
$\mathrm{OH}^{-}$
$\mathrm{NH}_{2}{ }^{-}$
$\mathrm{CO}_{3}{ }^{2-}$
$\mathrm{PO}_{4}{ }^{2-}$

## Brønsted-Lowry Acids and Bases

## Conjugate Acid-Base Pairs

## More examples



- $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(e) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})$ acid base conjugate conjugate acid base
- $\mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\ell) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{HCO}_{3}{ }^{-}(\mathrm{aq})$ acid base conjugate conjugate acid base


## Brønsted-Lowry Acids and Bases

## Relative Strengths of Acids and Bases

- Strong acids are completely dissociated in water.
- Their conjugate bases are quite weak.
- They are good proton donors.
- examples: $\mathrm{HCl}, \mathrm{HI}, \mathrm{HBr}, \mathrm{HNO}_{3}, \mathrm{H}_{2} \mathrm{SO}_{4}, \mathrm{HClO}_{4}$
- Example: $\mathrm{HCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})$

$$
\text { 1.2 M } \quad 1.2 \mathrm{M} \quad 1.2 \mathrm{M}
$$

- Acid fully dissociates. No equilibrium occurs between the acid and its ions.
- A large acid dissociation constant, $\mathrm{K}_{\mathrm{a}}$, is expected.
- $\mathrm{K}_{\mathrm{a}}$ is the equilibrium constant for the dissociation of an acid.


## Brønsted-Lowry Acids and Bases

## Relative Strengths of Acids and Bases

- Weak acids only dissociate partially in water.
- Their conjugate bases are weak bases.
- When weak acids are in solution, there is an equilibrium between the acid molecules and the constitute ions.
- Examples: $\mathrm{CH}_{3} \mathrm{COOH}, \mathrm{HNO}_{2}, \mathrm{H}_{2} \mathrm{CO}_{3}, \mathrm{H}_{3} \mathrm{BO}_{3}$, HF .
- Example:
$\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})$
- The $\mathrm{K}_{\mathrm{a}}$ is very small $\left(1.8 \times 10^{-5}\right)$.
- Some of the $\mathrm{CH}_{3} \mathrm{COOH}$ remains undissociated.


## Brønsted-Lowry Acids and Bases

## Relative Strengths of Acids and Bases

- Strong bases are completely dissociated in water.
- They have a great attraction to protons.
- They have a pair of electrons to form a bond with the proton.
- examples: $\mathrm{NaOH}, \mathrm{KOH}, \mathrm{Ca}(\mathrm{OH})_{2}, \mathrm{O}^{2-}, \mathrm{H}^{-}$
- Example:
$\mathrm{O}^{2-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{OH}^{-}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
- Expect a large base dissociation constant, $\mathrm{K}_{\mathrm{b}}$.
- $K_{b}$ is the equilibrium constant for the dissociation of a base.


## Brønsted-Lowry Acids and Bases

## Relative Strengths of Acids and Bases

- Weak bases are molecules or ions that are partially ionized in water to give OH -
- They are poor proton acceptors
- examples: $\mathrm{NH}_{3}, \mathrm{CH}_{3} \mathrm{CO}_{2}{ }^{-}$
- Example $\mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{OH}^{-}(\mathrm{aq})+\mathrm{NH}_{4}^{+}(\mathrm{aq})$
- The equilibrium constant, $\mathrm{K}_{\mathrm{b}}$, is small, $1.8 \times 10^{-5}$. Therefore the base is weak.
- Some $\mathrm{NH}_{3}$ molecules remain undissociated.


## Brønsted-Lowry Acids and Bases

## Relative Strengths of Acids and Bases

- Substances with negligible acidity such as $\mathrm{CH}_{4}$ do not dissociate in water.
- Their conjugate bases are exceedingly strong and react completely with water.


## Brønsted-Lowry Acids and Bases

## Relative Strengths of Acids and Bases

## Strong and weak vs concentrated and dilute

Do not confuse the meaning of the terms 'strong' and 'weak' with the terms 'concentrated' and 'dilute'.

Examples:
$1.0 \mathrm{M} \mathrm{HCl}=$ a concentrated solution of a strong acid.
$0.0001 \mathrm{M} \mathrm{HCl}=$ a dilute solution of a strong acid. 1.0 $\mathrm{M} \mathrm{HOAc}=$ a concentrated solution of a weak acid.
$0.001 \mathrm{M} \mathrm{HOAc}=$ a dilute solution of a weak acid.

## Brønsted-Lowry Acids and Bases

## Relative Strengths of Acids and Bases

- A strong acid has a weak conjugate base.
- The stronger the acid the weaker is its conjugate base.
- Very strong acids have conjugate bases with negligible base strength.
- The more easily an acid gives up a proton, the less easily its conjugate base accepts a proton.
- A strong base has a weak conjugate acid.
- The stronger the base the weaker is its conjugate acid.
- Very strong bases have conjugate acids with negligible acid strength.
- The more readily a base accepts a proton, the less easily its conjugate acid gives up a proton.


## Brønsted-Lowry Acids and Bases

## Relative Strengths of Acids and Bases

- A weak acid has a weak conjugate base.
- A weak acid only partially dissociates in aqueous solution.
- The conjugate base of a weak acid shows a slight ability to remove protons from water.



## Brønsted-Lowry Acids and Bases

## Relative Strengths of Acids and Bases

Which base is the weakest?

- $\mathrm{F}^{-}$
- $\mathrm{NH}_{3}$
- $\mathrm{OH}^{-}$
- $\mathrm{SO}_{4}{ }^{2-}$
- $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}^{-}$

ACID


## Brønsted-Lowry Acids and Bases

## Relative Strengths of Acids and Bases

Which acid is the strongest?

- $\mathrm{H}_{2} \mathrm{O}$
- $\mathrm{H}_{3} \mathrm{O}^{+}$
- HF
- $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$
- $\mathrm{NH}_{4}^{+}$


## The Autoionization of Water

- We have seen that water is amphoteric.
- In pure water, a few molecules act as bases and a few act as acids.
$\mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$ acid base conjugate conjugate acid base
- This is referred to as autoionization.
- $\mathrm{H}_{2} \mathrm{O}$ can therefore act as a Brønsted acid or base.
- At room temp. no molecules stay ionized for long.
- Thus pure water consists entirely of $\mathrm{H}_{2} \mathrm{O}$ molecules.


## The Autoionization of Water

## The Ion Product Constant

- The autoionization of water is an equilibrium process: $\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
- The equilibrium-constant expression for this process is:

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

- This special equilibrium constant is referred to as the ion-product constant for water, $K_{w}$.
- At 25 C,

$$
K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}
$$

## The Autoionization of Water

## The Ion Product Constant

In NEUTRAL solutions [ $\mathrm{H}+$ ] = [OH-]
In ACIDIC solutions [ $\mathrm{H}+$ ] > [OH-]
In BASIC solutions [OH-] > [H+]

## Acids and Bases

## Summary so far

- Acids - proton donors
- Bases - proton acceptors
- Weak acids and weak bases - partly dissociate
- Strong acids and strong bases - fully dissociate
- Conjugate acid-base pair - one H+ difference
- Autoionisation of water
$\mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
- $K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}$


## The pH Scale

- The concentration of $\mathrm{H}_{3} \mathrm{O}^{+}$or $\mathrm{OH}^{-}$in solution can vary over a wide range, but these concentrations are usually small.
- We define

$$
\begin{aligned}
\mathrm{pH} & =-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \\
\text {or } \mathrm{pH} & =-\log \left[\mathrm{H}^{+}\right]
\end{aligned}
$$

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

## The pH Scale

|  | Strongly <br> acidic | Neutral | Strongly <br> alkaline |
| :--- | :--- | :--- | ---: |
| $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$ | $10^{-1} \mathrm{M}$ | $10^{-7} \mathrm{M}$ | $10^{-14} \mathrm{M}$ |
| pH | $1 \longleftrightarrow$ | $7 \longrightarrow$ |  |

- In neutral water at $25^{\circ} \mathrm{C}, \mathrm{pH}=\mathrm{pOH}=7.00$.
- In acidic solutions, $\left[\mathrm{H}^{+}\right]>1.0 \times 10^{-7}$, so $\mathrm{pH}<7.00$.
- In basic solutions, $\left[\mathrm{H}^{+}\right]<1.0 \times 10^{-7}$, so $\mathrm{pH}>7.00$.
- The higher the pH , the lower the pOH , the more basic the solution.


## The pH Scale

| Solution Type | $\left[\mathbf{H}^{+}\right](\boldsymbol{M})$ | $\left[\mathrm{OH}^{-}\right](\boldsymbol{M})$ | pH Value |
| :--- | :--- | :--- | :--- |
| Acidic | $>1.0 \times 10^{-7}$ | $<1.0 \times 10^{-7}$ | $<7.00$ |
| Neutral | $=1.0 \times 10^{-7}$ | $=1.0 \times 10^{-7}$ | $=7.00$ |
| Basic | $<1.0 \times 10^{-7}$ | $>1.0 \times 10^{-7}$ | $>7.00$ |

- In pure water,

$$
K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.0 \times 10^{-14}
$$

- Because in pure water $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{OH}^{-}\right]$,

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left(1.0 \times 10^{-14}\right)^{1 / 2}=1.0 \times 10^{-7}
$$

## pH values of some common solutions



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## The pH Scale

## pOH and other " p " scales

- The " p " in pH tells us to take the negative log of the quantity (in this case, hydrogen ions).
- We can express concetration of $\mathrm{OH}^{-}$as pOH

$$
\begin{aligned}
\mathrm{pOH} & =-\log \left[\mathrm{OH}^{-}\right] \\
\mathrm{p} K_{w} & =-\log K_{w}
\end{aligned}
$$

## The pH Scale

## pOH and other " p " scales

Because at $25^{\circ} \mathrm{C}$,

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=K_{w}=1.0 \times 10^{-14},
$$

we know that

$$
-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]+-\log \left[\mathrm{OH}^{-}\right]=-\log K_{w}=14.00
$$

or, in other words,

$$
\mathrm{pH}+\mathrm{pOH}=\mathrm{p} K_{w}=14.00\left(\text { at } 25^{\circ} \mathrm{C}\right)
$$

## The pH Scale

## pOH and other " p " scales

## Exercise

Indicate whether solutions with each of the following ion concentrations are neutral, acidic, or basic:
(a) $\left[\mathrm{H}^{+}\right]=4 \times 10^{-9} \mathrm{M}$;
(b) $\left[\mathrm{OH}^{-}\right]=1 \times 10^{-7} \mathrm{M}$;
(c) $\left[\mathrm{OH}^{-}\right]=7 \times 10^{-13} \mathrm{M}$.

## The pH Scale

Exercise: What is the pH of an aqueous solution of $\left[\mathrm{OH}^{-}\right]$ $=1.0 \times 10^{-3} \mathrm{M}$ ?

1. 2.22
2. 3.00
3. 7.00
4. 10.78
5. 11.00

$$
\mathrm{pOH}=-\log \left(1.0 \times 10^{-3}\right)=3.00
$$

$$
\mathrm{pH}=14.00-\mathrm{pOH}
$$

$$
=14.00-3.00=11.00
$$

## The pH Scale

## Exercise:

If the pOH of a solution is 3.00 , what is the pH of the solution? Is the solution acidic or basic?

$$
\begin{gathered}
\mathrm{pH}+\mathrm{pOH}=\mathrm{p} K_{w}=14.00 \\
\mathrm{pH}=14.00-3.00=11.00 \\
\mathrm{pH}=11.00 \text { basic }
\end{gathered}
$$

## The pH Scale

## Measuring pH

- For less accurate measurements, one can use
- Litmus paper
- "Red" paper turns blue above $\sim \mathrm{pH}=8$
- "Blue" paper turns red below ~pH = 5
- An indicator
- Certain dyes change color as pH changes. These are indicators.
- Many indicators do not have a sharp color change as a function of pH .
- Most indicators tend to be red in more acidic solutions.


## The pH Scale

## Measuring pH

|  | pH range for color change |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 0 | 2 | $4$ |  | $6$ |  |  | 10 | 12 |  | 4 |
| Methyl violet | Yellow | Red | Vio |  |  |  |  |  |  |  |  |  |
| Thymol blue |  |  |  | Yellow |  |  | Yellow | Bl | Blue |  |  |  |
| Methyl orange |  |  | Re |  | Yello |  |  |  |  |  |  |  |
| Methyl red |  |  |  | Red |  | Y | Yellow |  |  |  |  |  |
| Bromthymol blue |  |  |  |  | Yellow |  | Bl | ue |  |  |  |  |
| Phenolphthalein |  |  |  |  |  |  | lorless |  | Pink |  |  |  |
| Alizarin yellow R |  |  |  |  |  |  |  | Yellow |  |  | Red |  |

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## The pH Scale

## Measuring pH

For more accurate measurements, one uses a pH meter, which measures the voltage in the solution.


## Strong Acids and Bases

## Strong acids

- Recall that strong acids e.g. $\mathrm{HCl}, \mathrm{HBr}, \mathrm{HI}, \mathrm{HNO}_{3}, \mathrm{H}_{2} \mathrm{SO}_{4}$, $\mathrm{HClO}_{3}$, and $\mathrm{HClO}_{4}$ dissociate completely to form $\mathrm{H}_{3} \mathrm{O}^{+}$.
- By definition, these are strong electrolytes and exist totally as ions in aqueous solution.
- Thus for the monoprotic strong acids,

$$
\begin{gathered}
{[\mathrm{acid}]=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]} \\
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] ; \mathrm{pH}+\mathrm{pOH}=14
\end{gathered}
$$

## Strong Acids and Bases

## Strong acids

## Exercise:

Calculate the pH of a solution made of 0.723 g perchloric acid in 500 mL of solution.

## Strong Acids and Bases

## Strong bases

- Strong bases also dissociate completely in aqueous solution.
- The pOH (and hence pH ) of a strong base is given by the initial molarity of the base.
- In order for a hydroxide to be a base, it must be soluble.
- Bases do not have to contain the $\mathrm{OH}^{-}$ion e.g. $\mathrm{O}^{2-}$
- As with strong acids, the calculation of pH for strong bases is simple.

$$
\begin{gathered}
{[\text { base }]=\left[\mathrm{OH}^{-}\right]} \\
\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right] ; \mathrm{pH}+\mathrm{pOH}=14
\end{gathered}
$$

## Strong Acids and Bases

## Strong bases

## Exercise

If 3.56 g of pure NaOH is dissolved in $10 \mathrm{dm}^{3}$ of water, what is the pH of the solution?

## Weak Acids

- Weak acids are only partially ionized in solution.
- There is a mixture of ions and unionized acid in solution.
- Therefore, weak acids are in equilibrium:

$$
\mathrm{HA}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{A}^{-}(a q)
$$



$$
\mathrm{HA}(a q) \rightleftharpoons \mathrm{H}^{+}(a q)+\mathrm{A}^{-}(a q)
$$



## Weak Acids

## Dissociation Constants

- For a generalized acid dissociation,

$$
\mathrm{HA}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{A}^{-}(a q)
$$

the equilibrium expression would be

$$
K_{c}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{A}^{-}\right]}{[\mathrm{HA}]}
$$

- This equilibrium constant is called the aciddissociation constant, $K_{a}$.


## Weak Acids

## Dissociation Constants

## The greater the value of $K_{a}$, the stronger the acid.

| Acid | Structural <br> Formula | Conjugate Base | Equilibrium Reaction | $K_{a}$ |
| :---: | :---: | :---: | :---: | :---: |
| Hydrofluoric (HF) | H-F | $\mathrm{F}^{-}$ | $\mathrm{HF}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{F}^{-}(a q)$ | $6.8 \times 10^{-4}$ |
| Nitrous $\left(\mathrm{HNO}_{2}\right)$ | $\mathrm{H}-\mathrm{O}-\mathrm{N}=\mathrm{O}$ | $\mathrm{NO}_{2}{ }^{-}$ | $\mathrm{HNO}_{2}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{NO}_{2}^{-}(a q)$ | $4.5 \times 10^{-4}$ |
| $\begin{aligned} & \text { Benzoic } \\ & \left(\mathrm{HC}_{7} \mathrm{H}_{5} \mathrm{O}_{2}\right) \end{aligned}$ |  | $\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{O}_{2}{ }^{-}$ | $\mathrm{HC}_{7} \mathrm{H}_{5} \mathrm{O}_{2}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{O}_{2}{ }^{-}(a q)$ | $6.3 \times 10^{-5}$ |
| Acetic $\left(\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}\right)$ |  | $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}$ | $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}(a q)$ | $1.8 \times 10^{-5}$ |
| Hypochlorous ( HClO ) | $\mathrm{H}-\mathrm{O}-\mathrm{Cl}$ | $\mathrm{ClO}^{-}$ | $\mathrm{HClO}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{ClO}^{-}(a q)$ | $3.0 \times 10^{-8}$ |
| Hydrocyanic (HCN) | $\mathrm{H}-\mathrm{C}=\mathrm{N}$ | $\mathrm{CN}^{-}$ | $\mathrm{HCN}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{CN}^{-}(a q)$ | $4.9 \times 10^{-10}$ |
| Phenol $\left(\mathrm{HC}_{6} \mathrm{H}_{5} \mathrm{O}\right)$ |  | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}^{-}$ | $\mathrm{HC}_{6} \mathrm{H}_{5} \mathrm{O}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}^{-}(a q)$ | $1.3 \times 10^{-10}$ |

*The proton that ionizes is shown in blue.

- If $K_{a} \gg 1$, then the acid is completely ionized and the acid is a strong acjd.


## Weak Acids

## Calculating $K_{a}$ from the pH

- Calculate $\mathrm{H}_{3} \mathrm{O}^{+}$and hence pH from $\mathrm{K}_{\mathrm{a}}$
- $\mathrm{K}_{\mathrm{a}}$ is usually small therefore use a approximation to simplify the problem.
- Test the assumption made.
- Use quadratic equation if " $x$ " is out by more the $5 \%$ of the original acid concentration.
- Calculate $\mathrm{K}_{\mathrm{a}}$ from pH


## Weak Acids

## Calculating $K_{a}$ from the pH

## Exercise:

The pH of a 0.10 M solution of formic acid, HCOOH , at 25 C is
2.38. Calculate $K_{a}$ for formic acid at this temperature.

- $\mathrm{HCOOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{aq}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{COO}^{-}(\mathrm{aq})$
- To calculate $K_{a}$, we need the equilibrium concentrations of all three species.
- We can find $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$, which is the same as $\left[\mathrm{HCOO}^{-}\right]$, from the pH .

$$
K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{HCOO}^{-}\right]}{[\mathrm{HCOOH}]}
$$

## Weak Acids

## Calculating $K_{a}$ from the pH

Weak acids are simply equilibrium calculations.

- The pH gives the equilibrium concentration of $\mathrm{H}^{+}$.
- Using $K_{a}$, the concentration of $\mathrm{H}^{+}$(and hence the pH ) can be calculated.
- Write the balanced chemical equation clearly showing the equilibrium.
- Write the equilibrium expression. Find the value for $K_{a}$.
- Write down the initial and equilibrium concentrations for everything except pure water.


## Weak Acids

## Calculating $K_{a}$ from the pH

$$
\begin{gathered}
K_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{HCOO}^{-}\right]}{[\mathrm{HCOOH}]} \\
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=2.38 \\
-2.38=\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-2.38}} \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{HCOO}^{-}\right]=4.2 \times 10^{-3} \mathrm{M}}
\end{gathered}
$$

Now we can set up a table...

## Weak Acids

## Calculating $K_{a}$ from the pH

$$
\mathrm{HCOOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{HCOO}^{-}(\mathrm{aq})
$$

[ HCOOH$], \mathrm{M} \quad\left[\mathrm{H}_{3} \mathrm{O}^{+}\right], \mathrm{M} \quad\left[\mathrm{HCOO}^{-}\right], \mathrm{M}$

| Initially | 0.10 | 0 | 0 |
| :--- | :---: | :---: | :---: |
| Change | $-4.2 \times 10^{-3}$ | $+4.2 \times 10^{-3}$ | $+4.2 \times 10^{-3}$ |
| At | $0.10-4.2 \times 10^{-3}$ | $4.2 \times 10^{-3}$ | $4.2 \times 10^{-3}$ |
| Equilibrium | $=0.0958 \sim 0.10$ |  |  |

$$
K_{a}=\frac{\left[4.2 \times 10^{-3}\right]\left[4.2 \times 10^{-3}\right]}{[0.10]}=1.8 \times 10^{-4}
$$

## Weak Acids

## Calculating $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and pH from Ka

## Example

What is the $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$in a 0.20 M solution of benzoic acid? $\left(K_{a}=6.3 \times 10^{-5}\right)$

Solution

- Benzoic acid, $\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{O}_{2} \mathrm{H}$
- We have a weak acid - does not fully dissociate
- We construct a table


## Weak Acids

## Calculating $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and pH from Ka

$$
\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{O}_{2} \mathrm{H}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{O}_{2}^{-}
$$

| Initially | 0.20 M | 0 M | 0 M |
| :--- | :--- | :--- | :--- |
| Change | -x | +x | +x |
| Equilibrium | $0.20-\mathrm{xM}$ | xM | xM |

$$
\begin{aligned}
\mathrm{K}_{\mathrm{a}}=\frac{\left.\left[\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{O}_{2}\right] \mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{C}_{7} \mathrm{H}_{5} \mathrm{O}_{2} \mathrm{H}\right]} & =6.3 \times 10^{-5} \\
\frac{(\mathrm{x})(\mathrm{x})}{(0.20-\mathrm{x})} & =6.3 \times 10^{-5}
\end{aligned}
$$

## Weak Acids

## Calculating $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and pH from Ka

This could be solved using a quadratic equation. But since this is a weak acid, we know that " $x$ " is very small, in fact much smaller than 0.20 M .

Therefore it is assumed that $(0.20-x) \cong 0.20$

## Weak Acids

## Calculating $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right.$] and pH from Ka

$$
\begin{aligned}
& \text { If } \begin{aligned}
& \frac{(x)(x)}{(0.20-x)}=6.3 \times 10^{-5} \\
& \text { and we assume }(0.20-x) \approx 0.20 \\
& \text { then, } \frac{x^{2}}{0.20}=6.3 \times 10^{-5} \\
& x=\sqrt{(0.20) \times\left(6.3 \times 10^{-5}\right)} \\
&=3.5 \times 10^{-3} \mathrm{M}
\end{aligned}
\end{aligned}
$$

Therefore, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=3.5 \times 10^{-3} \mathrm{M}$ $\mathrm{pH}=2.46$

## Weak Acids

## Calculating $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right.$] and pH from Ka

Test the assumption
$(0.20-X)=0.20-\left(3.5 \times 10^{-3}\right)$
$=0.196 \sim 0.20$ therefore assumption is valid
or
$\underline{3.5 \times 10^{-3} \mathrm{M}} \times 100=1.8 \%$ 0.20 M

## Weak Acids

## Calculating $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right.$] and pH from Ka

If the assumption is not valid, one must use the quadratic equation:

$$
x=\frac{-b \pm \sqrt{b^{2}-4 a c}}{2 a}
$$

## Weak Acids

## Calculating $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right.$] and pH from Ka

Guidelines on how to tackle the previous exercise

1) Write the ionization equilibrium of benzoic acid. If you don't know the actual formula of the acid use the general formula:

$$
\mathrm{HA}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\ell) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{A}^{-}(\mathrm{aq})
$$

2) Write the equilibrium constant expression using the given value of Ka.
3) Substitute the equilibrium concentrations into the equilibrium constant expression.
4) Simplify the equation by making an assumption.
5) Check the assumption.
6) If the quantity " $x$ " is more than about $5 \%$ of the concentration of the acid, use the quadratic equation.

## Weak Acids

## Calculating $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and pH from Ka

## Exercise:

Calculate the pH of $0.10 \mathrm{~mol} \mathrm{~L}^{-1} \mathrm{HF}$ solution
$\left(K_{a}=6.8 \times 10^{-4}\right)$.

## Weak Acids

## Percent lonization

- Magnitude of $\mathrm{K}_{\mathrm{a}}$ indicates the strength of a weak acid.
- Likewise percent ionization is a measure of acid strength.


## Percent Ionization $=\left[\mathrm{H}^{+}\right]_{\text {equilibrium }} \mathbf{x 1 0 0 \%}$ $[\mathrm{HA}]_{\text {initial }}$

- In the previous example

$$
\begin{aligned}
& {\left[\mathrm{H}^{+}\right]_{\mathrm{eq}}=4.2 \times 10^{-3} \mathrm{M}} \\
& {[\mathrm{HCOOH}]_{\text {initial }}=0.10 \mathrm{M}}
\end{aligned}
$$

Percent lonization $=\frac{4.2 \times 10^{-3}}{0.10} \times 100$
= 4.2\%

## Weak Acids

## Percent lonization


(a)

(b)
(a) The flask on the left contains $1 \mathrm{MHC} \mathrm{H}_{3} \mathrm{O}_{2}$; the one on the right contains 1 M HCl . Each balloon contains the same amount of magnesium metal. (b) When the $\mathbf{~ M g}$ metal is dropped into the acid, $\mathrm{H}_{2}$ gas is formed. The rate of $\mathrm{H}_{2}$ formation is higher for the $\mathbf{1 ~ M ~ H C l ~ s o l u t i o n ~ o n ~ t h e ~ r i g h t ~ a s ~ e v i d e n c e d ~ b y ~ m o r e ~ g a s ~ i n ~ t h e ~ b a l l o o n . ~}$

## Weak Acids

## Percent lonization

- Percent ionization relates the equilibrium $\mathrm{H}^{+}$ concentration, $\left[\mathrm{H}^{+}\right]_{\text {eqm }}$, to the initial HA concentration, $[\mathrm{HA}]_{0}$.
- The higher percent ionization, the stronger the acid.
- Percent ionization of a weak acid decreases as the molarity of the solution increases.


## Weak Acids

## Percent Ionization



For acetic acid 0.05 M solution is 2.0 \% ionized whereas a 0.15 M solution is $\mathbf{1 . 0}$ \% ionized.

## Weak Acids

## Polyprotic Acids

- Polyprotic acids have more than one ionizable H atom.
- The protons (H atoms) are removed in steps. For example:
$\mathrm{H}_{2} \mathrm{SO}_{3}(a q) \rightleftharpoons \mathrm{H}^{+}(a q)+\mathrm{HSO}_{3}^{-}(a q) \quad K_{a 1}=1.7 \times 10^{-2}$
$\mathrm{HSO}_{3}^{-}(a q) \rightleftharpoons \mathrm{H}^{+}(a q)+\mathrm{SO}_{3}^{2-}(a q) \quad K_{a 2}=6.4 \times 10^{-8}$
- It is always easier to remove the first proton in a polyprotic acid than the second.
- Therefore, $K_{a 1}>K_{a 2}>K_{a 3}$ etc.


## Weak Acids

## Polyprotic Acids

- If the difference between the $K_{a}$ for the first dissociation and subsequent $K_{a}$ values is $10^{3}$ or more, the pH generally depends only on the first dissociation.

| Name | Formula | $K_{a 1}$ | $K_{a 2}$ | $K_{a 3}$ |
| :--- | :--- | :--- | :--- | :--- |
| Ascorbic | $\mathrm{H}_{2} \mathrm{C}_{6} \mathrm{H}_{6} \mathrm{O}_{6}$ | $8.0 \times 10^{-5}$ | $1.6 \times 10^{-12}$ |  |
| Carbonic | $\mathrm{H}_{2} \mathrm{CO}_{3}$ | $4.3 \times 10^{-7}$ | $5.6 \times 10^{-11}$ |  |
| Citric | $\mathrm{H}_{3} \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{7}$ | $7.4 \times 10^{-4}$ | $1.7 \times 10^{-5}$ | $4.0 \times 10^{-7}$ |
| Oxalic | $\mathrm{H}_{2} \mathrm{C}^{-7} \mathrm{O}_{4}$ | $5.9 \times 10^{-2}$ | $6.4 \times 10^{-5}$ |  |
| Phosphoric | $\mathrm{H}_{3} \mathrm{PO}_{4}$ | $7.5 \times 10^{-3}$ | $6.2 \times 10^{-8}$ | $4.2 \times 10^{-13}$ |
| Sulfurous | $\mathrm{H}_{2} \mathrm{SO}_{3}$ | $1.7 \times 10^{-2}$ | $6.4 \times 10^{-8}$ |  |
| Sulfuric | $\mathrm{H}_{2} \mathrm{SO}_{4}$ | Large | $1.2 \times 10^{-2}$ |  |
| Tartaric | $\mathrm{H}_{2} \mathrm{C}_{4} \mathrm{H}_{4} \mathrm{O}_{6}$ | $1.0 \times 10^{-3}$ | $4.6 \times 10^{-5}$ |  |

## Weak Acids

## Summary so far



Calculate pH - weak acid $\rightarrow$ Equilibrium equation

$$
\rightarrow \mathrm{K}_{\mathrm{a}} \rightarrow \mathrm{pH}
$$

$[\rightarrow$ Assumption
$\{\rightarrow$ If not valid, use

- quadratic equation.
(next)
$\rightarrow$ Calculate $\mathrm{K}_{\mathrm{a}}$ from pH .


## Weak Bases

- Weak bases react with water to remove protons from water.
- There is an equilibrium between the base and the resulting ions:

$$
\begin{aligned}
& \text { Weak base }+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \text { conjugate acid }+\mathrm{OH}^{-} \\
& \mathrm{NH}_{3}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{NH}_{4}^{+}(a q)+\mathrm{OH}^{-}(a q)
\end{aligned}
$$

add $\mathrm{H}^{+}$


## Weak Bases

- The equilibrium constant expression for a weak base is

$$
K_{b}=\frac{[\mathrm{HB}]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{B}^{-}\right]}
$$

where $K_{b}$ is the base-dissociation constant.
$K_{b}$ can be used to find $\left[\mathrm{OH}^{-}\right]$and, consequently, pH .

## Weak Bases

|  | Lewis <br> Base | Conjugate <br> Acid | Equilibrium Reaction | $\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{4}{ }^{+}+\mathrm{OH}^{-}$ |
| :--- | :--- | :--- | :--- | :--- |

## Weak Bases

## Types of Weak Bases

1. Neutral (uncharged) substances that have an atom with a nonbonding pair of electrons that can accept a proton.
Examples:

- Ammonia - : $\mathrm{NH}_{3}$
- Amines

| $\mathrm{CH}_{3} \ddot{\mathrm{~N}} \mathrm{H}_{2}$ | primary amine |
| :--- | :--- |
| $\mathrm{CH}_{3} \dot{\mathrm{~N}} \mathrm{HCH}_{3}$ | secondary amine |
| $\mathrm{CH}_{3}-\stackrel{\mathrm{N}}{ } \mathrm{CH}_{3}$ | tertiary amine |
| $\mathrm{CH}_{3}$ |  |

## Weak Bases

## Types of Weak Bases

2. The conjugate bases (anions) of weak acids.

- Acetate ion, $\mathrm{CH}_{3} \mathrm{COO}^{-}$- conjugate base of acetic acid.

Example: in sodium acetate, $\mathrm{CH}_{3} \mathrm{COONa}$.

- Hypochlorite ion, $\mathrm{ClO}^{-}$- conjugate base of
hypochlorous acid.
Example: in calcium hypochlorite, $\mathrm{Ca}(\mathrm{ClO})_{2}$
- Carbonates, bicarbonates, phosphates.

3. Alkaloids.

Naturally occurring basic substances
e.g. cocaine, ephedrine, quinine, mescaline, morphine

## Weak Bases

## pH of Basic Solutions

Example: What is the pH of a 0.15 M solution of $\mathrm{NH}_{3}$ ?
Solution:

$$
\begin{gathered}
\mathrm{NH}_{3}(a q)+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{NH}_{4}^{+}(a q)+\mathrm{OH}^{-}(a q) \\
K_{b}=\frac{\left[\mathrm{NH}_{4}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{3}\right]}=1.8 \times 10^{-5}
\end{gathered}
$$

Tabulate the data...

## Weak Bases

## pH of Basic Solutions

$\left[\mathrm{NH}_{3}\right], M \quad\left[\mathrm{NH}_{4}^{+}\right], M\left[\mathrm{OH}^{-}\right], M$

| Initially | 0.15 | 0 | 0 |
| :--- | :---: | :---: | :---: |
| Change | -x | $+x$ | $+x$ |
| At Equilibrium | $0.15-x \approx 0.15$ | $x$ | $x$ |

## Weak Bases

## pH of Basic Solutions

$$
1.8 \times 10^{-5}=\frac{(x)^{2}}{(0.15)}
$$

$$
\left(1.8 \times 10^{-5}\right)(0.15)=x^{2}
$$

$$
2.7 \times 10^{-6}=x^{2}, x=1.6 \times 10^{-3}
$$

Test the assumption: Percent ionization $=(0.0016 / 0.15) \times 100 \%$ = $1.07 \%$

Or $0.15-x=0.15-0.0016=0.1484$

## Weak Bases

## pH of Basic Solutions

Therefore,

$$
\begin{aligned}
& {\left[\mathrm{OH}^{-}\right]=1.6 \times 10^{-3} \mathrm{M}} \\
& \mathrm{pOH}=-\log \left(1.6 \times 10^{-3}\right) \\
& \mathrm{pOH}=2.80 \\
& \mathrm{pH}=14.00-2.80 \\
& \mathrm{pH}=11.20
\end{aligned}
$$

## Relationship between $K_{a}$ and $K_{b}$

- When two reactions are added to give a third, the equilibrium constant for the third reaction is the product of the equilibrium constants for the first two:

Reaction $1+$ Reaction $2=$ Reaction 3
has

$$
\mathrm{K}_{3}=\mathrm{K}_{1} \times \mathrm{K}_{2}
$$

## Relationship between $K_{a}$ and $K_{b}$

- $K_{a}$ and $K_{b}$ are related in this way:

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

- Therefore, if you know one of them, you can calculate the other.
- For a conjugate acid-base pair $K_{w}=K_{a} \times K_{b}$
- The larger the $K_{a}$, the smaller the $K_{b}$. That is, the stronger the acid, the weaker the conjugate base.
- In terms of $\mathrm{pK}_{\mathrm{a}}$ and $\mathrm{pK}_{\mathrm{b}}$

$$
p K_{w}=p K_{a}+p K_{b}=14 \quad\left(\text { at } 25^{\circ} \mathrm{C}\right)
$$

## Relationship between $K_{a}$ and $K_{b}$

| Acid | $K_{a}$ | Base | $\boldsymbol{K}_{\boldsymbol{b}}$ |
| :--- | :--- | :--- | :--- |
| $\mathrm{HNO}_{3}$ | $($ Strong acid $)$ | $\mathrm{NO}_{3}{ }^{-}$ | $($Negligible basicity) |
| HF | $6.8 \times 10^{-4}$ | $\mathrm{~F}^{-}$ | $1.5 \times 10^{-11}$ |
| $\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}$ | $1.8 \times 10^{-5}$ | $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{O}_{2}{ }^{-}$ | $5.6 \times 10^{-10}$ |
| $\mathrm{H}_{2} \mathrm{CO}_{3}$ | $4.3 \times 10^{-7}$ | $\mathrm{HCO}_{3}$ | $2.3 \times 10^{-8}$ |
| $\mathrm{NH}_{4}^{+}$ | $5.6 \times 10^{-10}$ | $\mathrm{NH}_{3}$ | $1.8 \times 10^{-5}$ |
| $\mathrm{HCO}_{3}{ }^{-}$ | $5.6 \times 10^{-11}$ | $\mathrm{CO}_{3}{ }^{2-}$ | $1.8 \times 10^{-4}$ |
| $\mathrm{OH}^{-}$ | $($Negligible acidity) | $\mathrm{O}^{2-}$ | (Strong base) |

## Acid-Base Properties of Solutions

- Nearly all salts are strong electrolytes.
- Therefore, salts exist entirely of ions in solution.
- Acid-base properties of salts are a consequence of the reaction of their ions in solution.
- The reaction in which ions produce $\mathrm{H}^{+}$or $\mathrm{OH}^{-}$in water is called hydrolysis.
- Anions from weak acids are basic.
- Anions from strong acids are neutral.


## Acid-Base Properties of Solutions

## Reactions of Anions with Water

- In general, anions, $X^{-}$, are bases in solution i.e. can be considered as the conjugate base of an acid.
- E.g. $\mathrm{Cl}^{-}$is the conjugate base of $\mathrm{HCl}, \mathrm{CH}_{3} \mathrm{COO}^{-}$is the conjugate base of $\mathrm{CH}_{3} \mathrm{COOH}$.
- As such, anions can react with water in a hydrolysis reaction to form $\mathrm{OH}^{-}$and the conjugate acid:

$$
\mathrm{X}^{-}(a q)+\mathrm{H}_{2} \mathrm{O}(I) \rightleftharpoons \mathrm{HX}(a q)+\mathrm{OH}^{-}(a q)
$$

## Acid-Base properties of Solutions

## Reactions of Cations with Water

- Cations with acidic protons (like $\mathrm{NH}_{4}{ }^{+}$) will lower the pH of a solution.
- They can be considered as the conjugate acids of weak bases.
- $\mathrm{NH}_{4}{ }^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons \mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$
- Most metal cations that are hydrated in solution also lower the pH of the solution.


## Acid-Base Properties of Solutions

## Combined Effect of Cation and Anion in Solution

1. An anion that is the conjugate base of a strong acid will not affect the pH . Example, $\mathrm{Br}^{-}$
2. An anion that is the conjugate base of a weak acid will increase the pH . Example, $\mathrm{CN}^{-}$
3. A cation that is the conjugate acid of a weak base will decrease the pH. Example, $\mathrm{CH}_{3} \mathrm{NH}_{3}{ }^{+}$

## Acid-Base Properties of Solutions

## Combined Effect of Cation and Anion in Solution

4. Cations of the strong Arrhenius bases will not affect the pH .
5. Other metal ions will cause a decrease in pH .
6. When a solution contains both the conjugate base of a weak acid and the conjugate

(a)

(b)

(c) acid of a weak base, the affect on pH depends on the $K_{a}$ and $K_{b}$ values.

## Acid-Base Behaviour and Chemical Structure

- In this section we discuss briefly the effects of chemical structure on acid base behavior.
- An acid must contain at least one $H$ bonded to an $X$ atom, i.e. $\mathrm{H}-\mathrm{X}$
- Three factors affect the strengths of acids


## Acid-Base Behaviour and Chemical Structure

## Factors that Affect Acid Strength

(i) Polarity of the $\mathrm{H}-\mathrm{X}$

- $\mathrm{H}-\mathrm{X}$ bond must be polar with $\mathrm{H} \delta+$ and $\mathrm{X} \delta$ -

$$
\overrightarrow{\mathrm{H}-\mathrm{X}}
$$

-The more polar the bond, the stronger the acid.

- If $X$ is a metal then the bond polarity is $H \delta-, X \delta+$ and the substance is a base, the $\mathrm{H}-\mathrm{X}$ bond must be weak enough to be broken, the conjugate base, X -, must be stable.


## Acid-Base Behaviour and Chemical Structure

## Factors that Affect Acid Strength

(ii) The Strength of the bond

- Release of a proton implies the breaking of the X-H bond.
- The weaker the bond stronger the acid.
- The H-F bond is the most polar. However it has the highest bond strength amongst the hydrogen halides, hence it is a weak acid.


## Acid-Base Behaviour and Chemical Structure

## Factors that Affect Acid Strength

(iii) Stability of the conjugate base, $X^{-}$

- The conjugate base, $X^{-}$, must be stable.
- Any feature that lowers the energy of the conjugate base in comparison with the acid increases its stability.
- The greater the stability of the conjugate base, the stronger the acid.

The strength of an acid is often a combination of the polarity of the $\mathrm{H}-\mathrm{X}$ bond, the strength of the $\mathrm{H}-\mathrm{X}$ bond, and the stability of the conjugate base, $X$.

## Acid-Base Behaviour and Chemical Structure

## Binary Acids

- Binary acids contain H and just one other element. E.g. HF, $\mathrm{H}_{2} \mathrm{~S}, \mathrm{HI}, \mathrm{HCl}$, etc.
- The more polar the $\mathrm{H}-\mathrm{X}$ bond and/or the weaker the $\mathrm{H}-\mathrm{X}$ bond, the more acidic the compound.



## Increasing acid strength

Increasing base strength

## Acid-Base Behaviour and Chemical Structure

## Binary Acids

## Which acid is the strongest?

- $\mathrm{H}_{2} \mathrm{~S}$
- HF
- HCl
- HBr
- HI

|  |  |  |  |  | 18 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 3A | 4A | 5A | 6A | 7A | 2 |
| 13 | 14 | 15 | 16 | 17 | He |
| 5 | 6 | 7 | 8 | 9 | 10 |
| B | C | N | O | F | Ne |
| 13 | 14 | 15 | 16 | 17 | 18 |
| Al | Si | P | S | Cl | Ar |
| 31 | 32 | 33 | 34 | 35 | 36 |
| Ga | Ge | As | Se | Br | Kr |
| 49 | 50 | 51 | 52 | 53 | 54 |
| In | Sn | Sb | Te | I | Xe |
| 81 | 82 | 83 | 84 | 85 | 86 |
| Tl | Pb | Bi | Po | At | Rn |
| 113 | 114 | 115 | 116 |  |  |

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## Acid-Base Behaviour and Chemical Structure

## Binary Acids

## Which base is the strongest?

- $\mathrm{ClO}_{4}^{-}$
- $\mathrm{BrO}_{3}^{-}$
- $\mathrm{BrO}_{4}^{-}$
- $1 \mathrm{O}_{3}{ }^{-}$
- $\mathrm{IO}_{4}^{-}$

|  |  |  |  | $\begin{aligned} & 8 \mathrm{~A} \\ & 18 \end{aligned}$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{aligned} & 3 \mathrm{~A} \\ & 13 \end{aligned}$ | $\begin{aligned} & 4 \mathrm{~A} \\ & 14 \end{aligned}$ | $\begin{aligned} & 5 \mathrm{~A} \\ & 15 \end{aligned}$ | $\begin{aligned} & 6 \mathrm{~A} \\ & 16 \end{aligned}$ | $\begin{gathered} 7 \mathrm{~A} \\ 17 \end{gathered}$ | $\begin{gathered} 2 \\ \mathrm{He} \end{gathered}$ |
| 5 | 6 | 7 | 8 | 9 | 10 |
| B | C | N | O | F | Ne |
| 13 | 14 | 15 | 16 | 17 | 18 |
| Al | Si | P | S | Cl | Ar |
| 31 | 32 | 33 | 34 | 35 | 36 |
| Ga | Ge | As | Se | Br | $\mathbf{K r}$ |
| 49 | 50 | 51 | 52 | 53 | 54 |
| In | Sn | Sb | Te | I | Xe |
| 81 | 82 | 83 | 84 | 85 | 86 |
| T1 | Pb | Bi | Po | At | Rn |
| 113 | 114 | 115 | 116 |  |  |

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## Acid-Base Behaviour and Chemical Structure

## Binary Acids

- Acid strength increases across a period and down a group.
- Conversely, base strength decreases across a period and down a group.
- HF is a weak acid because the bond energy is high.
- The electronegativity difference between C and H is so small that the $\mathrm{C}-\mathrm{H}$ bond is non-polar and $\mathrm{CH}_{4}$ is neither an acid nor a base.


## Acid-Base Behaviour and Chemical Structure

## Oxyacids

- Oxyacids contain O-H bonds (and often also =O groups).
- Exmaple: sulphuric acid.

- All oxyacids have the general structure $\mathrm{Y}-\mathrm{O}-\mathrm{H}$.
- The strength of the acid depends on $Y$ and the atoms attached to Y . The OH group/s in these molecules can ionise as follows:

$$
\lambda \mathrm{Y}-\mathrm{O}-\mathrm{H} \longrightarrow \geqslant \mathrm{Y}-\mathrm{O}^{-}+\mathrm{H}^{+}
$$

## Acid-Base Behaviour and Chemical Structure

## Oxyacids

- This only happens in practice if the atom Y is a strongly electronegative atom, e.g., P, S, N, etc. Atom Y can then attract electron density towards itself, thereby polarising the $\mathrm{O}-\mathrm{H}$ bond and facilitating ionisation:
- If $Y$ is a metal (low electronegativity), then the substances are bases.
- If Y has intermediate electronegativity (e.g. I, EN = 2.5), the electrons are between Y and O and the substance is a weak oxyacid.


## Acid-Base Behaviour and Chemical Structure

## Oxyacids

- If Y has a large electronegativity (e.g. $\mathrm{Cl}, \mathrm{EN}=3.0$ ), the electrons are located closer to Y than O and the $\mathrm{O}-\mathrm{H}$ bond is polarized to lose $\mathrm{H}^{+}$.

Shift of electron density


## Acid-Base Behaviour and Chemical Structure

## Oxyacids

## Summary

1. For oxyacids that have the same number of OH groups and the same number of O atoms, acid strength increases with increasing electronegativity of the central atom.
H-O-Y

| Acid | EN of $\mathbf{Y}$ | $\boldsymbol{K}_{\boldsymbol{a}}$ |
| :--- | :--- | :--- |
| HClO | 3.0 | $3.0 \times 10^{-8}$ |
| HBrO | 2.8 | $2.5 \times 10^{-9}$ |
| HIO | 2.5 | $2.3 \times 10^{-11}$ |

## Acid-Base Behaviour and Chemical Structure

## Oxyacids

## Summary

2. For a series of oxyacids that have the same central atom $Y$, acidity increases with the number of oxygen atoms attached to Y increases.

| Hypochlorous | Chlorous | Chloric | Perchloric |
| :---: | :---: | :---: | :---: |
| $\mathrm{H}-\ddot{\mathrm{O}}-\ddot{\mathrm{Cl}}:$ | $\mathrm{H}-\ddot{\mathrm{O}}-\ddot{\mathrm{C}} \mathrm{l}-\ddot{\mathrm{O}}:$ | $\mathrm{H}-\ddot{\mathrm{O}}-\mathrm{Cl}-\ddot{\mathrm{O}}:$ | $\mathrm{H}-\ddot{\mathrm{O}}:$ |
| $K_{a}=3.0 \times 10^{-8}$ | $K_{a}=1.1 \times 10^{-2}$ | Strong acid | Strong acid |
|  | Increasing acid strength |  |  |

## Acid-Base Behaviour and Chemical Structure

## Carboxylic Acids

- Carboxylic acids are organic acids that contain the carboxyl group:



Acetic acid

- Often written as -COOH or as $-\mathrm{CO}_{2} \mathrm{H}$.
- All carboxylic acids are weak acids.
- When the carboxylic acid loses a proton, it generate the carboxylate anion, $\mathrm{COO}^{-}$.


Formic acid


Benzoic acid
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## Acid-Base Behaviour and Chemical Structure

## Carboxylic Acids

- It is of interest to note that methanol, $\mathrm{CH}_{3} \mathrm{OH}$, does not have acidic properties in water, while acetic acid [ $\mathrm{CH}_{3} \mathrm{COOH}$ ] does. Why?
- Compare the molecular structures:

methanol

acetic acid


## Acid-Base Behaviour and Chemical Structure

## Carboxylic Acids

Two factors contribute to acidic behaviour of carboxylic acids:

1. Additional O atom attached to the carbon attracts electron density from the $\mathrm{O}-\mathrm{H}$ bond increasing its polarity and stabilising the conjugate base
2. Resonance in the conjugate bases of carboxylic acids stabilizes the base and makes the conjugate acid more acidic.


## Acid-Base Behaviour and Chemical Structure

## Carboxylic Acids

- The acid strength of carboxylic acids also increases as the number of electronegative atoms in the molecule increases.
- Example:

acetic acid

$$
K_{a}=1.8 \times 10^{-5}
$$



Trifluoroacetic acid
$K_{a}=0.50$

## Lewis Acids and Bases

- In previous sections we discussed Brønsted-Lowry acids and bases.
- In the Brønsted-Lowry view, an acid is a proton donor. When a proton is donated to another molecule, where does it actually go on the acceptor molecule ?
- It invariably goes onto a lone pair of electrons situated on some atom (e.g., a N or O -) belonging to the base.


## Lewis Acids and Bases

- G.N. Lewis proposed that what was characteristic of acids and bases wasn't so much that a proton is always exchanged between an acid and a base, but that a lone pair of electrons is always involved.
- This led to the definition of Lewis acids and bases.
- According to the Lewis view:


## A Lewis acid is an electron pair acceptor. A Lewis base is electron pair donor.

- Note: Lewis acids and bases do not need to contain protons. Therefore, the Lewis definition is the most general definition of acids and bases.


## Lewis Acids



- Lewis acids are defined as electron-pair acceptors.
- Atoms with an empty valence orbital can be Lewis acids.
- Lewis acids generally have an incomplete octet e.g. $\mathrm{BF}_{3}$
- Compounds with $\pi$-bonds can act as Lewis acids.


## Lewis Bases



## Lewis Lewis base acid

- Lewis bases are defined as electron-pair donors.
- Anything that could be a Brønsted-Lowry base is a Lewis base.
- Lewis bases can interact with things other than protons, however.


## Metal Complexes

- A central metal atom bonded to a group of molecules or ions is a metal complex e.g. $\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}\right]^{+}$.
- If the complex bears a charge, it is a complex ion.
- Compounds containing complexes are coordination compounds.



## Metal Complexes

## The metal-ligand bond

- The molecules or ions that bond to the metal ion in a complex are known as ligands.
- They are usually anions or polar molecules. They have at least one unshared pair of valence electrons.
- Examples of ligands:





## Metal Complexes

## The metal-ligand bond

- The bond between a ligand and a metal ion is an example of an interaction between a Lewis base and acid.
- The ligands have nonbonding electrons and are Lewis bases.
- The metal has empty orbitals and is a Lewis acid.
- A metal-ligand bond is formed between the Lewis acid (metal) and the Lewis base (ligand).



## End of Chapter 16

## Acid-Base Equilibria

