## Acid-Base Character of Salt Solutions

The pH of a salt solution will depend on the acidbase nature of both the cation and anion.

## Cations

Cations are potentially acidic, but some have no effect on pH .
$\mathrm{M}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{n+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{M}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5} \mathrm{OH}^{(n-1)+}$
$\checkmark$ Metal cations with high charge density are acidic in water; e.g., $\mathrm{Al}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}, \mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}$.
$\checkmark$ Metal cations with low charge density are neutral in water, e.g., $\mathrm{Na}^{+}, \mathrm{K}^{+}, \mathrm{Rb}^{+}, \mathrm{Cs}^{+}, \mathrm{Sr}^{2+}, \mathrm{Ba}^{2+}$.
$\checkmark$ Polyatomic cations that are conjugate acids of molecular weak bases are acidic; e.g., $\mathrm{NH}_{4}{ }^{+}$, $\mathrm{CH}_{3} \mathrm{NH}_{2}{ }^{+}$.

## Acid-Base Character of Salt Solutions <br> Anions

Anions that are not acid anions are potentially basic, but some have no effect on pH .

$$
\mathrm{X}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HX}+\mathrm{OH}^{-}
$$

$\checkmark$ Aprotic conjugate bases of weak acids are basic in water; e.g., $\mathrm{OAc}^{-}, \mathrm{OCl}^{-}, \mathrm{F}^{-}, \mathrm{NO}_{2}^{-}, \mathrm{CN}^{-}, \mathrm{SO}_{4}{ }^{2-}$, $\mathrm{SO}_{3}{ }^{2-}, \mathrm{CO}_{3}{ }^{2-}$.
$\checkmark$ Aprotic conjugate bases of strong acids are neutral in water; e.g., $\mathrm{Cl}^{-}, \mathrm{Br}^{-}, \mathrm{I}^{-}, \mathrm{NO}_{3}^{-}, \mathrm{ClO}_{4}^{-}$.

## Acid-Base Character of Acid Anions

Acid anions (which are generally amphiprotic) may be acidic or basic, depending on the relative magnitudes of their $K_{a}$ and $K_{b}$ values.
$\checkmark$ If $K_{a}>K_{b}$, the acid anion will be acidic; e.g., $\mathrm{HSO}_{4}^{-}, \mathrm{HSO}_{3}^{-}, \mathrm{H}_{2} \mathrm{PO}_{4}^{-}$
$\checkmark$ If $K_{b}>K_{a}$, the acid anion will be basic; e.g., $\mathrm{HCO}_{3}^{-}, \mathrm{HS}^{-}, \mathrm{HPO}_{4}^{-}$

## Reactions Between Two Conjugate Acid-Base Pairs

What happens when two solutions, each containing different conjugate acid-base pairs, are mixed together?
$\checkmark$ The two acids will compete to donate protons, and the two bases will compete to accept protons.

An equilibrium will be established between the stronger acid and the stronger base in the direction favoring formation of the weaker conjugate base and weaker conjugate acid.

$$
\mathrm{HCl}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{Cl}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

Acid strengths: $\mathrm{HCl}>\mathrm{H}_{3} \mathrm{O}^{+}$
Base strengths: $\mathrm{H}_{2} \mathrm{O}>\mathrm{Cl}^{-}$
$\Rightarrow$ Equilibrium lies right.

$$
\mathrm{HOAc}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{OAc}^{-}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

Acid strengths: $\mathrm{H}_{3} \mathrm{O}^{+}>\mathrm{HOAc}$
Base strengths: $\mathrm{OAc}^{-}>\mathrm{H}_{2} \mathrm{O}$
$\Rightarrow$ Equilibrium lies left.

# Predicting Reactions with an <br> Ordered Acid-Base Table 

The favored equilibrium will be between the acid that lies higher in the left column and the base that lies lower in the right column, to produce the conjugates in the upper right and lower left.


## pH After Neutralization

The reaction of an acid with a stoichiometrically equivalent amount of a base is called neutralization.
$\checkmark$ The pH of the solution following a neutralization depends upon the acid and base strengths of the products of the reaction, which in turn depend upon the acid and base strengths of the original reactants.

## Strong Acid + Strong Base

The reaction is between the hydronium ion produced by the acid and the hydroxide ion produced by the base.

For any strong acid-strong base neutralization, the net ionic equation is

$$
\mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}
$$

Neutralization produces a neutral solution ( $\mathrm{pH}=7$ ).

Example: $\mathrm{HNO}_{3}(a q)+\mathrm{NaOH}(a q)$
Molecular equation:
$\mathrm{HNO}_{3}(a q)+\mathrm{NaOH}(a q) \rightarrow \mathrm{H}_{2} \mathrm{O}(l)+\mathrm{NaNO}_{3}(a q)$
Ionic equation:

$$
\begin{aligned}
\mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{NO}_{3}^{-}(a q) & +\mathrm{Na}^{+}(a q)+\mathrm{OH}^{-}(a q) \\
& \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(l)+\mathrm{Na}^{+}(a q)+\mathrm{NO}_{3}^{-}(a q)
\end{aligned}
$$

Net ionic equation:

$$
\mathrm{H}_{3} \mathrm{O}^{+}(a q)+\mathrm{OH}^{-}(a q) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(l)
$$

## Weak Acid + Strong Base

All of the weak acid is converted into an equivalent amount of its conjugate base, which is basic.

Neutralization produces a basic solution ( $\mathrm{pH}>7$ ).
Example:
Molecular equation:

$$
\mathrm{HOAc}(a q)+\mathrm{NaOH}(a q) \rightarrow \mathrm{H}_{2} \mathrm{O}(l)+\mathrm{NaOAc}(a q)
$$

Ionic equation:

$$
\begin{aligned}
\mathrm{HOAc}(a q)+\mathrm{Na}^{+}(a q) & +\mathrm{OH}^{-}(a q) \\
\rightarrow & \mathrm{H}_{2} \mathrm{O}(l)+\mathrm{Na}^{+}(a q)+\mathrm{OAc}^{-}(a q)
\end{aligned}
$$

Net ionic equation:

$$
\mathrm{HOAc}(a q)+\mathrm{OH}^{-}(a q) \rightarrow \mathrm{H}_{2} \mathrm{O}(l)+\mathrm{OAc}^{-}(a q)
$$

The back reaction to the neutralization produces the basic pH :
$\mathrm{OAc}^{-}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HOAc}+\mathrm{OH}^{-}$

$$
K_{b}\left(\mathrm{OAc}^{-}\right)=K_{w} / K_{a}(\mathrm{HOAc})=5.65 \times 10^{-10}
$$

## Weak Base + Strong Acid

All of the weak base is converted into an equivalent amount of its conjugate acid, which is acidic.

Neutralization produces an acidic solution $(\mathrm{pH}<7)$.
Example:
Molecular equation:

$$
\mathrm{NH}_{3}(a q)+\mathrm{HCl}(a q) \rightarrow \mathrm{NH}_{4} \mathrm{Cl}(a q)
$$

Ionic equation:

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

Net ionic equation:

$$
\mathrm{NH}_{3}(a q)+\mathrm{H}_{3} \mathrm{O}^{+}(a q) \rightarrow \mathrm{NH}_{4}^{+}(a q)+\mathrm{H}_{2} \mathrm{O}(l)
$$

The back reaction to the neutralization produces the acidic pH :
$\mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+}$

$$
K_{a}\left(\mathrm{NH}_{4}^{+}\right)=K_{w} / K_{b}\left(\mathrm{NH}_{3}\right)=5.65 \times 10^{-10}
$$

## Neutralization Between a Weak Acid and Weak Base

The pH of the resulting solution will depend upon the relative magnitudes of the $K_{b}$ and $K_{a}$ of the conjugates produced in the neutralization.

The resulting species with the larger $K$ value will determine whether the solution is acidic or basic.

$$
\begin{array}{llll}
\mathrm{HF}(a q)+ & \mathrm{NH}_{3}(a q) & \rightleftharpoons & \mathrm{F}^{-}(a q) \\
K_{a}= & K_{b}= & K_{b}= & \mathrm{NH}_{4}^{+}(a q) \\
6.8 \times 10^{-4} & 1.8 \times 10^{-5} & 1.5 \times 10^{-11} & 5.6 \times 10^{-10} \\
& \\
& K_{a}\left(\mathrm{NH}_{4}^{+}\right)>K_{b}\left(\mathrm{~F}^{-}\right) \Rightarrow \mathrm{pH}<7
\end{array}
$$

