## Chemistry 30

## Acids \& Bases

Properties of Acids (\& Bases)

- dissolve in $\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$
- blue litmus $\rightarrow$ red (or red litmus $\rightarrow$ blue)
- taste sour (taste bitter)
- react with $\mathrm{Mg}, \mathrm{Zn}$ to form $\mathrm{H}_{2}(\mathrm{~g})$
- neutralize bases (neutralize acids)
- conduct


## Arrhenius Definition of Acids and Bases

- all acids produce hydrogen ions $\left(\mathrm{H}^{+}(\mathrm{aq})\right)$ when dissolved in water
- all bases produce hydroxide ions $\left(\mathrm{OH}^{-}(\mathrm{aq})\right)$ when dissolved in water
- the properties of acids and bases are due to the $\mathrm{H}^{+}(\mathrm{aq})$ and $\mathrm{OH}^{-}(\mathrm{aq})$ produced
- all neutral substances that are neutral are neutral because they don't produce $\mathrm{H}^{+}(\mathrm{aq})$ when dissolved

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ex: }\mp@subsup{\textrm{HNO}}{3}{(aq)}->\mp@subsup{\textrm{H}}{}{+}(\textrm{aq})+\mp@subsup{\textrm{NO}}{3}{-}(\textrm{aq}
- acid
    NaOH(aq)}->\mp@subsup{\textrm{Na}}{}{+}(\textrm{aq})+\mp@subsup{\textrm{OH}}{}{-}(\textrm{aq}
    - base
    LiCl(aq) }->\mp@subsup{\textrm{Li}}{}{+}(\textrm{aq})+\mp@subsup{\textrm{Cl}}{}{-}(\textrm{aq})\quad-neutral
BUT! Na2}\mp@subsup{\textrm{CO}}{3}{(}(\textrm{aq})->2\mp@subsup{\textrm{Na}}{}{+}(\textrm{aq})+\mp@subsup{\textrm{CO}}{3}{2-}(\textrm{aq})\quad\mathrm{ - not neutral!!! (basic)
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The Arrhenius definition isn't enough to explain all acidic \& basic substances

## Bronsted-Lowry Acids and Bases

- an acid is a proton donor (i.e. $\mathrm{H}^{+}$donor)
- a base is a proton acceptor (i.e. $\mathrm{H}^{+}$acceptor) - must have an lone electron pair to accept the proton
- an acid can only behave like an acid if there's a base present to accept the $\mathrm{H}^{+}$ion (when HCl is dissolved in water, it behaves like an acid, but in a nonpolar solvent, HCl is NOT an acid)
- water can behave as both a proton donor (acid) and a proton acceptor (base) - the positive hydrogen ion is attracted to the negative lone pair, and "bonds" to the water molecule instead of the chloride ion, forming the $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ (hydronium ion) - water is acting as a proton acceptor (base), and $\mathrm{HCl}(\mathrm{aq})$ is the proton donor (acid)

- water can also behave as a proton donor (base), for example with ammonia $\left(\mathrm{NH}_{3}\right)$

- Brønsted-Lowry acids and bases always come in pairs - termed conjugate pairs
- when a BL acid (in this case $\mathrm{H}_{2} \mathrm{O}$ ) donates its proton, it becomes a BL base $\left(\mathrm{OH}^{-}\right)$, the "conjugate base" of water. The pair, $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{OH}^{-}$are called a "conjugate acid-base pair"
- $\mathrm{NH}_{3}$ behaves as a BL base (accepting a proton), its conjugate acid is $\mathrm{NH}_{4}^{+}$

These reactions are really equilibrium reactions:
$\underset{\text { BL-base }}{\mathrm{NH}_{3}(\mathrm{~g})}+\underset{\text { BL-acid }}{\mathrm{H}-\mathrm{OH}(\mathrm{l})} \rightleftharpoons \quad \underset{\text { BL-acid }}{\mathrm{NH}_{4}^{+}(\mathrm{aq})}+\underset{\text { BL-base }}{\mathrm{OH}^{-}(\mathrm{aq})}$

- when a base accepts a proton $\rightarrow$ acid (conjugate acid)
- when an acid donates a proton $\rightarrow$ base (conjugate base)
- conjugate acid-base pair - differ only by ONE $\mathrm{H}^{+}$ion
- conjugate base always has a charge -1 compared to its conjugate acid
- $\boldsymbol{\uparrow}$ strength of the acid, $\downarrow$ strength of the conjugate base


## Weak and Strong Acids

- Just like many other reactions, not all acids and bases will completely dissociate - but reach equilibrium instead $\rightarrow$ Ka (just a special case of Keq for acids, Kb for bases)

$$
\begin{array}{ll}
\mathrm{HCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq}) & \mathrm{Ka}=\underset{* *}{1.3 \times 10^{6} \text { strong acid }} \text { (almost all products) } \\
\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftarrows \mathrm{CH}_{3} \mathrm{COO}-(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) & \mathrm{Ka}=\underset{* *}{1.8 \times 10-5 \text { (very few products) }} \text { weak acid }
\end{array}
$$

- the stronger the acid, the more likely it is to give up a proton (same with bases, the stronger the base, the more likely it is to accept a proton)
- strength has NOTHING to do with the concentration of the acid (or base)
p. 11 in the data booklet -strongest acids are at the top left of the table (个个 Ka-100\% ionization) -strongest bases are at the bottom left of the table ( $\downarrow \downarrow \mathrm{Ka}$ - means favours the reverse reaction)
- There are only 6 "strong" acids; the "strong" bases are any soluble hydroxides (salts with $\mathrm{OH}^{\text {- }}$ ions that dissolve in water)
- strong acids and bases ionize $100 \%$ (no equilibrium) (ex: $\mathrm{HCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})$ )
- weak acids and bases ionize < 100\% (equilibrium) (ex: $\mathrm{HF}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{F}(\mathrm{aq})$ )
- conjugates of the strong acids and bases are SO weak, they will not ionize at all (this is true for all of the 6 strong acids and the soluble hydroxides)
(ex: $\mathrm{Cl}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \leftarrow \mathrm{HCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ so no reaction- this reaction will not take place in the forward direction)
- the stronger an acid, the weaker its conjugate base (and vice versa)


## Acidity/Basicity of Salts (Salt Hydrolysis)

- a salt is an ionic compound
- whether a salt is acidic, basic or neutral depends on whether the ions that form the salt behave as BL acids, BL bases or neither
- each ion acts independently

$$
\begin{aligned}
& \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftarrows \mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \\
& (\mathrm{BL}-\mathrm{A}) \\
& \mathrm{Cl}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \leftarrow \text { no reaction } \\
& \text { (neutral) }
\end{aligned}
$$

$$
\begin{aligned}
& \mathrm{CO}_{3}^{2-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftarrows \mathrm{HCO}_{3}^{-}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \\
& (\mathrm{BL}-\mathrm{B})
\end{aligned}
$$

$\mathrm{Na}^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow$ no reaction
(if an ion isn't on p.11, assume it is a spectator)

- $\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{aq})$ in water, the $\mathrm{NH}_{4}^{+}(\mathrm{aq})$ behaves as a BL acid, the $\mathrm{Cl}(\mathrm{aq})$ as a BL neutral, so overall, the salt will be an acid
- $\mathrm{NaCl}(\mathrm{aq})$ in water, the $\mathrm{Na}^{+}(\mathrm{aq})$ is neutral, the $\mathrm{Cl}^{-}(\mathrm{aq})$ is neutral, so the salt is neutral
- $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{CO}_{3}(\mathrm{aq})$ in water, the $\mathrm{NH}_{4}{ }^{+}(\mathrm{aq})$ is an acid, the $\mathrm{CO}_{3}{ }^{2-}(\mathrm{aq})$ is a base, so the salt will be CLOSE (not precisely) to neutral


## Writing Bronsted-Lowry reactions between acids and bases

- So far, we've looked only at how acids, bases and salts behave in water
- Brønsted-Lowry theory allows for acid base reactions both with water and in the absence of water
- using Bronsted-Lowry theory, we can write net ionic equations for the reaction taking place and indicate the position of the equilibrium


## ex: A solution of $\mathrm{KOH}(\mathrm{aq})$ is reacted with a solution of $\mathrm{NaHCO}_{3}(\mathrm{aq})$

## Steps

1. list all of the ions produced (for weak acids or insoluble compounds - write them in their PREDOMINANT form the undissociated form)
 $\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ and $\mathrm{HCO}_{3}^{-}(\mathrm{aq})$ appear on both sides of p .11 's table (they can behave as both acid or base - called amphiprotic or amphoteric - they must be considered as both)
2. identify the strongest acid (SA) - closest to the top of p.11's table on the left side, and strongest base (SB) closest to the bottom of the table on the right side - the SA and $S B$ will be the first to react with each other - they are most likely to donate and accept a proton
3. Write the NET equation - just the reaction between the SA and $S B$ (leave out all of the spectator ions) - transfer a $\longrightarrow \mathrm{HCO}_{3}^{-}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightleftarrows \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{CO}_{3}{ }^{2-}(\mathrm{aq})$
proton from the $S A$ to the $S B$
4. Predict the equilibrium status (which, forward or reverse predominates - look at the two acids, $\mathrm{HCO}_{3}^{-}(\mathrm{aq})$ and $\mathrm{H}_{2} \mathrm{O}(I)$ (on the product side) - whichever acid is stronger (higher on p.11)pushes the equilibrium away by donating a proton
ex: Predict the reaction between $\mathrm{HCl}(\mathrm{aq})$ and $\mathrm{NaC}_{6} \mathrm{H}_{5} \mathrm{COO}(\mathrm{aq})$

split $\mathrm{HCl}(\mathrm{aq})$ into $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ and $\mathrm{Cl}^{-}(\mathrm{aq})$ because $\mathrm{HCl}(\mathrm{aq})$ is a strong acid ( $100 \%$ ionization). Split $\mathrm{NaC}_{6} \mathrm{H}_{5} \mathrm{COO}$ (aq) because it is soluble ( $100 \%$ dissociation)
ex: $\mathrm{NaOH}(\mathrm{aq})$ in $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$
$\mathrm{Na}^{+}(\mathrm{aq}), \mathrm{OH}^{-}(\mathrm{aq}), \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}), \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$

- $\quad \mathrm{SB} \quad \mathrm{SA} \quad \mathrm{A} / \mathrm{B}$
$\mathrm{OH}^{-}(\mathrm{aq})+\underset{\substack{\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \\ \text { products favored }} \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})}{ }+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
$\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ is NOT split up because it is a weak acid -Ka is very small, so most of the $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ is found undissociated, so it is written as is


## ex: $\mathrm{NH}_{3}(\mathrm{aq})$ in $\mathrm{HNO}_{3}(\mathrm{aq})$

$\mathrm{NH}_{3}(\mathrm{~g}), \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}), \mathrm{NO}_{3}{ }^{-}(\mathrm{aq}), \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
$\begin{array}{llll}\text { SB } & \text { SA } & B & A / B\end{array}$

$$
\mathrm{NH}_{3}(\mathrm{~g})+\underset{\text { products favored }}{\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \underset{\mathrm{NH}_{4}^{+}}{ }(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

## Polyprotic/Polybasic Acids and Bases

- acids (or bases) that can lose (or gain) more than one proton per molecule
- dibasic/diprotic (two protons): $\mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq}), \mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq}), \mathrm{H}_{2} \mathrm{SO}_{3}(\mathrm{aq})$
- tribasic/triprotic (three protons): $\mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{aq}), \mathrm{H}_{3} \mathrm{BO}_{3}(\mathrm{aq})$
- the first proton is the "easiest" to gain (or lose) (Ka or Kb is the largest)
- others are harder because of the charge (a polyprotic acid that has lost a proton will already have a negative charge and will not lose another proton as easily because of the charge)
** not all molecules that have more than one hydrogen are polyprotic (ex: organic acids)


## ex: Write the ionization steps for $\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})$

$\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{HSO}_{4}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$
$\mathrm{HSO}_{4}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftarrows \mathrm{SO}_{4}{ }^{2-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$
(this step is one way because $\mathrm{H}_{2} \mathrm{SO}_{4}$ is strong) (this is equilibrium because $\mathrm{HSO}_{4}{ }^{-}$is not strong)
ex: $\mathrm{NH}_{2}{ }^{-}(\mathrm{aq})$ is dibasic. Write its ionization steps
$\mathrm{NH}_{2}{ }^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftarrows \mathrm{NH}_{3}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
$\mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftarrows \mathrm{NH}_{4}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
pH - The scale, what it means, and calculations

- $\mathrm{pH}=$ the "power" (exponent) of hydrogen (1909)
- developed to easily compare acidity and basicity
- an difference in pH of one is a difference in concentration of 10 (difference of $3=1000 \mathrm{x}$ concentration)

$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]$
$\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}(\mathrm{aq})\right]$
$10^{-\mathrm{pH}}=\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]$
$10^{-\mathrm{pOH}}=\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$
pH and pOH are related through the ionization constant of water (more on this later), by:

$$
\mathrm{pH}+\mathrm{pOH}=14.00 \quad\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=1.00 \times 10^{-14}
$$

ex: What is the pH of a solution of $\mathrm{HCl}(\mathrm{aq})$ if its concentration is $3.00 \times 10^{-2} \mathrm{~mol} / \mathrm{L}$ ?
Since $\mathrm{HCl}(\mathrm{aq})$ is a strong acid: $\mathrm{HCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq}) \quad$ (this is $100 \%$ reaction)
therefore $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]=[\mathrm{HCl}(\mathrm{aq})]=3.00 \times 10^{-2} \mathrm{~mol} / \mathrm{L} \quad \mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]$

$$
\begin{aligned}
& \text { SD rules: } \\
& \text { in pH only the numbers after the decimal count } \\
& \text { (numbers before come from the exponent- if you } \\
& \text { remember vour loa math so don't count) }
\end{aligned}
$$

$$
\begin{aligned}
& =-\log \left(3.00 \times 10^{-2}\right) \\
& =1.523
\end{aligned}
$$

ex: What is the pH of $0.00453 \mathrm{~mol} / \mathrm{L} \mathrm{NaOH}(\mathrm{aq})$ ?
Since $\mathrm{NaOH}(\mathrm{aq})$ is soluble: $\quad \mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{Na}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \quad$ (this is $100 \%$ reaction)
therefore $\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=0.00453 \mathrm{~mol} / \mathrm{L}$

$$
\begin{aligned}
\mathrm{pOH} & =-\log \left[\mathrm{OH}^{-}(\mathrm{aq})\right] \\
& =-\log (0.00453) \\
& =2.344 \\
\mathrm{pH} & =14.00-2.344 \\
& =11.656(\text { keep } 3 \text { SD) }
\end{aligned}
$$

ex: Calculate the pH if 4.75 g of $\mathrm{NaOH}(\mathrm{s})$ is dissolved in water to make 750 mL of solution

Find $[\mathrm{NaOH}]$ first, then [ $\mathrm{OH}^{-}(\mathrm{aq})$ ], then from this, pOH and finally pH

$$
\frac{4.75 \mathrm{~g}}{} \times \frac{1 \mathrm{~mol}}{40.00 \mathrm{~g}} \times \frac{1}{0.750 \mathrm{~L}}=0.158 \mathrm{~mol} / \mathrm{LNaOH}
$$

Since $[\mathrm{NaOH}(\mathrm{aq})]$ is soluble, $[\mathrm{NaOH}(\mathrm{aq})]=\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=0.158 \mathrm{~mol} / \mathrm{L}$

$$
\begin{aligned}
\mathrm{pOH} & =-\log \left[\mathrm{OH}^{-}(\mathrm{aq})\right] \\
& =-\log (0.158) \\
& =0.800(\text { (if you rounded in the middle, it would be } 0.801) \\
\mathrm{pH} & =14.00-0.800=13.200
\end{aligned}
$$

ex: Calculate the mass of $\mathrm{HCl}(\mathrm{g})$ required to make 500 mL of a solution with a pOH of 12.00

$$
\begin{array}{ll}
\begin{array}{ll}
\mathrm{pOH} & =12.00 \\
\mathrm{pH} & = \\
& =14.00-12.00=2.00 \\
{\left[\begin{array}{rl}
{\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]} & = \\
= & 10^{-(2.00)} \\
= & 1.00
\end{array}\right.} \\
\times 10^{-2} \mathrm{~mol} / \mathrm{L}
\end{array} \\
\begin{aligned}
\frac{1.0 \times 10^{-2} \mathrm{~mol}}{\mathrm{~L}}
\end{aligned} & \times \frac{0.500 \mathrm{~L}}{1} \times \frac{36.46 \mathrm{~g}}{1 \mathrm{~mol}}=0.18 \mathrm{~g}
\end{array}
$$

This one is exactly the opposite- from pOH , find pH , then find $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]$, then $[\mathrm{HCl}]$, and finally mass
ex: Calculate the $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]$ in a solution made from $2.50 \mathrm{~g} \mathrm{Ba}(\mathrm{OH})_{2}$ dissolved to make 450 mL of solution at $25^{\circ} \mathrm{C}$.

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Find [OH]}]\mathrm{ , then use
[H3\mp@subsup{O}{}{+}][OH}]=1.00\times1\mp@subsup{0}{}{-14}\mathrm{ to 
determine [H3O}\mp@subsup{}{}{+}]\mathrm{ (don't forget
2OH
```

$$
\begin{aligned}
& \frac{2.50 \mathrm{gBa}(\mathrm{OH})_{2}}{} \times \frac{1 \mathrm{~mol}}{171.35 \mathrm{~g}} \times \frac{2 \mathrm{molOH}^{-}}{1 \mathrm{molBa}(\mathrm{OH})_{2}} \times \frac{1}{0.450 \mathrm{~L}}=0.0648 \mathrm{~mol} / \mathrm{LOH}^{-} \\
& \begin{aligned}
1.00 \times 10^{-14} & =\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right] \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] } & =\frac{1.00 \times 10^{-14}}{\left[\mathrm{OH}^{-}\right]} \\
& =\frac{1.00 \times 10^{-14}}{0.0648} \\
& =1.54 \times 10^{-13} \mathrm{~mol} / \mathrm{L}
\end{aligned}
\end{aligned}
$$

## Calculations Involving Weak Acids and Weak Bases

- pH and pOH calculations can be performed for weak acids and bases as well, but must include provisions for the equilibrium that is set up because of the strength of the acid/base
ex: $0.100 \mathrm{~mol} / \mathrm{L} \mathrm{HCl}(\mathrm{aq})$

$$
\begin{aligned}
& \mathrm{HCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{Cl}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \\
& 0.100 \mathrm{~mol} / \mathrm{L} \rightarrow
\end{aligned} \quad 0.100 \mathrm{~mol} / \mathrm{L}(100 \% \text { reaction })
$$

$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]$
$=1.000$
$0.100 \mathrm{~mol} / \mathrm{L} \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$

$$
\begin{gathered}
\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \underset{<0.100 \mathrm{~mol} / \mathrm{L}}{\rightleftarrows} \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \\
\hline 0 .
\end{gathered}
$$

$0.100 \mathrm{~mol} / \mathrm{L}$
$\rightleftarrows$

$$
\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]
$$

$=$ much more than 1.000 since not all of the acid dissociates
${ }^{* *}$ weak acids will have a higher pH than a strong acid at the same concentration
${ }^{* *} \boldsymbol{\uparrow}$ acid strength $\rightarrow \uparrow \mathrm{Ka} \rightarrow \boldsymbol{\downarrow} \mathrm{pH}$

Calculations involving weak acids (or bases) include $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right],\left[\mathrm{OH}^{-}(\mathrm{aq})\right], \mathrm{Ka}($ or Kb$), \mathrm{pH}$ and pOH
ex: In a $0.100 \mathrm{~mol} / \mathrm{L}$ solution of propanoic acid, the hydronium ion concentration is found to be $1.16 \times 10^{-3} \mathrm{~mol} / \mathrm{L}$. Calculate the ionization constant ( Ka, or Keq ) for propanoic acid.

Solve this the way you would solve a Keq problem - you need [eq] - use an ICE chart! - since they gave us $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]$, we can fill in $[I]$, and $[\mathrm{E}]$, then work backwards to fill in the rest of the [E]s

This should remind you of equilibrium - there is nothing new, just now it's always acids and bases

|  | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftarrows$ | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ | Start here, then fill |
| :--- | :--- | :--- | :--- |
| [I] | $0.100 \mathrm{~mol} / \mathrm{L}$ | 0 | 0 |
| [C] | $-\left(1.16 \times 10^{-3}\right)$ | $+\left(1.16 \times 10^{-3}\right)$ | $+\left(1.16 \times 10^{-3}\right)$ |
| [E] $0.099 \mathrm{~mol} / \mathrm{L}$ | $1.16 \times 10^{-3} \mathrm{~mol} / \mathrm{L}$ | $1.16 \times 10^{-3} \mathrm{~mol} / \mathrm{L}$ |  |

$$
\begin{aligned}
\mathrm{Ka} & =\frac{\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COOH}\right]} \\
& =\frac{\left(1.16 \times 10^{-3}\right)\left(1.16 \times 10^{-3}\right)}{(0.099)} \\
& =1.36 \times 10^{-5}
\end{aligned}
$$

ex: What is the pH of a $0.100 \mathrm{~mol} / \mathrm{L}$ solution of $\operatorname{HCN}(\mathrm{aq})$ ?
$\mathrm{HCN}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftarrows \quad \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{CN}^{-}(\mathrm{aq})$
[I] $0.100 \mathrm{~mol} / \mathrm{L}$
[C] -x
[E] $(0.100-x) \mathrm{mol} / \mathrm{L}$
$+x \quad+x$
$x \mathrm{~mol} / \mathrm{L} \quad \mathrm{xmol} / \mathrm{L}$
to solve for pH , you need to solve for $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]$. This is just like the equilibrium unit, solve an ICE chart for x , this will give you $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]$, then you can use $\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$

$$
\mathrm{Ka}=\frac{\left[\mathrm{CN}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{[\mathrm{HCN}]}
$$

to solve this without the quadratic equation, the approximation must be used:
$1000 \times \mathrm{Ka}<0.100$ ?
$1000\left(6.2 \times 10^{-10}\right)<0.100$
therefore $\mathrm{x} \approx 0$
therefore $0.100-\mathrm{x} \approx 0.100$
$\mathrm{x}=\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]=7.9 \times 10^{-6} \mathrm{~mol} / \mathrm{L}$
$\therefore \mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]$
$=-\log \left(7.9 \times 10^{-6}\right)$
$=5.10$
ex: Determine the initial concentration of an acetic acid solution if its $\mathbf{p H}$ is $\mathbf{2 . 5 0}$.

$$
\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftarrows \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})
$$

[I] $\times \mathrm{mol} / \mathrm{L}$
0
[C] $-\left(3.2 \times 10^{-3}\right)$
[E] $\mathrm{x}-3.2 \times 10^{-3} \mathrm{~mol} / \mathrm{L}$
$\stackrel{+\left(3.2 \times 10^{-3}\right)}{+\left(3.2 \times 10^{-3}\right)}$
$3.2 \times 10^{-3} \mathrm{~mol} / \mathrm{L} \quad 3.2 \times 10^{-3} \mathrm{~mol} / \mathrm{L}$

$$
\mathrm{Ka}=\frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}
$$

$$
1.8 \times 10^{-5}=\frac{\left(3.2 \times 10^{-3}\right)\left(3.2 \times 10^{-3}\right)}{\left(\mathrm{x}-3.2 \times 10^{-3}\right)}
$$

$$
1.8 \times 10^{-5} x-5.7 \times 10^{-8}=1.0 \times 10^{-5}
$$

$$
1.85 \times 10^{-5} x=1.0 \times 10^{-5}
$$

$$
x=0.56
$$

$$
\therefore\left[\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})\right]=0.56 \mathrm{~mol} / \mathrm{L}
$$

## Just another look at $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right],\left[\mathrm{OH}^{-}(\mathrm{aq})\right]$.....

Don't you think it's rather strange that when an acid dissolves in water and donates its proton, it creates $\mathrm{OH}^{-}(\mathrm{aq})$ ?
(in case you've forgotten): $0.100 \mathrm{~mol} / \mathrm{L} \mathrm{HCl}(\mathrm{aq}) \rightarrow 0.100 \mathrm{~mol} / \mathrm{L} \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$
and since $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=1.00 \times 10^{-14}$
then $\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=1.00 \times 10^{-14} / 0.100=1.00 \times 10^{-13} \mathrm{~mol} / \mathrm{L}$
Really, acids don't create $\mathrm{OH}^{-}(\mathrm{aq})$, they just affect the equilibrium that already exists in the water where they are dissolved:

$$
\begin{aligned}
\mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftarrows \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \quad \mathrm{Ka} & =\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]\left[\mathrm{OH}^{-}(\mathrm{aq})\right] \\
& =1.00 \times 10^{-14}
\end{aligned}
$$

(at $25^{\circ} \mathrm{C}$, in pure water, $\left[\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})\right]=\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=\sqrt{1.00 \times 10^{-14}}=1.00 \times 10^{-7} \mathrm{~mol} / \mathrm{L}$ )

According to LeChatelier, if $\uparrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ (by adding an acid), then the equilibrium will shift $\leftarrow$, reducing the [ $\left.\mathrm{OH}^{-}(\mathrm{aq})\right]$ already present to maintain $\mathrm{Keq}(\mathrm{Ka})$.

Since Ka is a constant $\left(1.00 \times 10^{-14}\right)$ at $25^{\circ} \mathrm{C}$, then if one of either $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ or $\mathrm{OH}^{-}(\mathrm{aq})$ is increased, then the other will decrease.

This equilibrium allows us to perform similar calculations for weak bases that we can for weak acids, even though our Ka table (on p.11) only has Ka values.

## The Relationship between Ka and Kb

Looking at the weak acid, $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ and its conjugate base, $\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})$, we can examine the relationship between Ka and Kb .
acetic acid: $\quad \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftarrows \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$
$\mathrm{Ka}=\frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}$
acetate ion:


Although at first glance, the two don't seem related $(\mathbf{K a}=\mathbf{1} / \mathbf{K b})$, they are related through Kw (the equilibrium constant for water:

$$
\frac{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]} \times \frac{\left[\mathrm{CH}_{3} \mathrm{COOH}^{2}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{COO}\right]}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=\mathrm{Kw}
$$

So: $\quad \mathbf{K a x ~ K b}=\mathbf{K w}$
From this relationship, you can calculate $\mathrm{Kb}(\mathrm{Kb}=\mathrm{Kw} / \mathrm{Ka})$, where at $25^{\circ} \mathrm{C}, \mathrm{Kw}=1.00 \times 10^{-14}$
ex: Calculate the Kb for $\mathrm{NH}_{3}(\mathrm{aq})$
From p.11, Ka for $\mathrm{NH}_{4}^{+}(\mathrm{aq})$ is $5.8 \times 10^{-10}$

$$
\begin{aligned}
\mathrm{Ka} \times \mathrm{Kb} & =\mathrm{Kw} \\
\mathrm{~Kb} & =\frac{\mathrm{Kw}}{\mathrm{Ka}} \\
& =\frac{1.00 \times 10^{-14}}{5.8 \times 10^{-10}} \\
& =1.7 \times 10^{-5}
\end{aligned}
$$

Once Kb is determined, all of the calculations performed for weak acids can be done for weak bases too.
ex: Calculate the pH of a $0.100 \mathrm{~mol} / \mathrm{L}$ solution of $\mathrm{NaCH}_{3} \mathrm{COO}(\mathrm{aq})$.
this is solved exactly the same way as if it were a weak acid, except that in the ICE chart, $\mathrm{OH}^{-}$is present (instead of $\mathrm{H}_{3} \mathrm{O}^{+}$), we must find Kb (not just look it up), and when finding pH , we have to find pOH first.
[I] $\begin{aligned} & \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq}) \\ & 0.100 \mathrm{~mol} / \mathrm{L}\end{aligned}$
0
$+X$
X
[C] -x
[E] 0.100 - x mol/L
$\mathrm{Kb}=\frac{\left[\mathrm{CH}_{3} \mathrm{COOH}^{2}\left[\mathrm{OH}^{-}\right]\right.}{\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}$

Kb was solved above using $\mathrm{KaxKb}=\mathrm{Kw}$ $5.6 \times 10^{-10}=\frac{x^{2}}{0.100-x}$
$5.6 \times 10^{-10}=x^{2}$
$7.5 \times 10^{-6}=x$

$$
\begin{aligned}
& \mathrm{x}=\left[\mathrm{OH}^{-}(\mathrm{aq})\right] 7.5 \times 10^{-6} \mathrm{~mol} / \mathrm{L} \\
& \begin{aligned}
\therefore \mathrm{pOH} & =-\log \left[\mathrm{OH}^{-}(\mathrm{aq})\right] \\
& =-\log \left(7.5 \times 10^{-6}\right) \\
& =5.13
\end{aligned}
\end{aligned}
$$

$\mathrm{pOH}+\mathrm{pH}=14.00$
$\therefore \mathrm{pH}=14.00-5.13=8.87$

## ex: Calculate Kb for an unknown base if a $0.225 \mathrm{~mol} / \mathrm{L}$ solution has a pH of 9.98 .

let $A^{-}(a q)$ be the unknown base:
from pH , find pOH and then $\mathrm{OH}^{-}(\mathrm{aq})$ so you can fill in part of the ICE chart \& work backwards
$\mathrm{A}^{-}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftarrows \quad \mathrm{HA}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq})$
0.225
[I] 0.2250 .0
$[C] 0.225-9.5 \times 10^{-5} \quad+9.5 \times 10^{-5} \quad+9.5 \times 10^{-5}$
[E] 0.225

$\mathrm{pH}+\mathrm{pOH}=14.00$
$\mathrm{pOH}=14.00-9.98=4.02$
$\left[\mathrm{OH}^{-}(\mathrm{aq})\right]=10^{-\mathrm{pOH}}$


$$
=4.1 \times 10^{-8}
$$

## Buffers

A buffer is a solution that will resist changes in pH when either an acid or a base is added. Buffers are used wherever a specific pH must be maintained - some examples are in the body (the blood buffers), in pools and hot tubs (to allow the chemicals to work properly inhibiting the growth of algae and other organisms) and fish tanks.

There are two basic types of buffers:

## Solutions of strong concentrated acids (or strong concentrated bases)

- resist changes in pH when acids are added because they already have such a low pH
- resist changes in pH when (small amounts of) bases are added because they neutralize


## Solutions that are able to neutralize both acids or bases

- there are two types of this variety of buffer - solutions of amphiprotic (amphoteric) substances (like $\mathrm{HCO}_{3}{ }^{-}(\mathrm{aq})$, or a solution of a weak acid and its conjugate base together $\left(\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})\right.$ and $\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})$ often in equal quantities).

These solutions behave as buffers because they are able to remove the excess ions that will lead to a change in $\mathrm{pH}, \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ or $\mathrm{OH}^{-}(\mathrm{aq})$.
ex: In a buffer solution of $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ and $\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq}), \mathrm{HCl}(\mathrm{aq})$ was added. Why is the pH not changed noticeably?
examine the situation using $B-L$ equations:

| $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}), \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})$, | $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}), \mathrm{Cl}^{-}(\mathrm{aq}), \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ |  |
| :---: | :---: | :---: |
| SB | SA | $\mathrm{A} / \mathrm{B}$ |

$$
\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \rightleftarrows \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq}) \quad \text { equilibrium } \rightarrow \text { is favoured }
$$

- since the forward reaction is favoured, most of the reactants (most of the $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ ) becomes products, and since most of the $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ is removed, the pH is not affected greatly.
ex: similarily, when $\mathrm{NaOH}(\mathrm{aq})$ is added:

$\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \rightleftarrows \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq}) \quad$ equilibrium $\rightarrow$ is favoured
- since the forward reaction is favoured, most of the reactants (most of the $\mathrm{OH}^{-}(\mathrm{aq})$ ) becomes products, and since most of the $\mathrm{OH}^{-}(\mathrm{aq})$ is removed, the pH is not affected greatly.


## Buffers in the Body

The body must maintain a pH of approximately 7.35 to keep enzymes and proteins from denaturing. If proteins and enzymes denature, they cannot function, and the body's cells (and eventually the body) die. The two buffers in the blood are $\mathrm{HCO}_{3}{ }^{-}(\mathrm{aq})$ and $\mathrm{HPO}_{4}{ }^{2-}(\mathrm{aq})$.

The acid that must be buffered is $\mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq})$, which is produced naturally as $\mathrm{CO}_{2}(\mathrm{~g})$ produced by the body's cells during cellular respiration is carried by the blood's plasma to be excreted in the lungs. The level of $\mathrm{CO}_{2}(\mathrm{~g})$, and hence $\mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq})$ is constantly changing as we take breaths and exhale. Our body's buffer system must be constantly adjusting to maintain a narrow pH range.
ex: as someone holds their breath (suffocates), what happens to maintain pH in the body?
$\uparrow \mathrm{CO}_{2}(\mathrm{~g}) \rightarrow \uparrow \mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq}) \rightarrow \uparrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \rightarrow \boldsymbol{\mathrm { pH }} \rightarrow$ protein denaturation $\rightarrow$ cell death
the increase in $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ affects the following buffer system:

$$
\mathrm{HPO}_{4}{ }^{2-}(\mathrm{aq})+\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \rightleftarrows \mathrm{H}_{2} \mathrm{O}(\mathrm{I})+\mathrm{H}_{2} \mathrm{PO}^{-}(\mathrm{aq}) \quad \text { the equilibrium is shifted } \rightarrow \text { due to } \uparrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})
$$ $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ is consumed, pH remains steady

ex: if someone hyperventilates, what happens to maintain the pH in their body?
$\downarrow \mathrm{CO}_{2}(\mathrm{~g}) \rightarrow \downarrow \mathrm{H}_{2} \mathrm{CO}_{3}(\mathrm{aq}) \rightarrow \downarrow \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq}) \rightarrow \uparrow \mathrm{pH} \rightarrow$ protein denaturation $\rightarrow$ cell death
The decrease in $\mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})$ will cause the opposite shift in the equilibrium system described above.

## Calculating the pH of a buffer system

Calculating the pH of a buffer is not unlike the other calculations. The only difference is that they are made with some acid and its conjugate base to start with (both product and reactant are present initially).
ex: (equal amounts of acid and conjugate base) Calculate the resulting pH of a buffer consisting of $0.100 \mathrm{~mol} / \mathrm{L}$ each of $\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})$ and its conjugate base $\mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})$.


