WATER CHEMISTRY

- The self-ionization of water has a small equilibrium constant. What does this imply?

THE CONCENTRATION OF HYDROXIDE AND HYDRONIUM ION IN PURE WATER IS VERY SMALL!

How small?

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

m pure water, the concentration of hydroxide and hydronium must be equal, since they are formed at the same time and at the same ratio from the ionization reaction of water.

$$
K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1 \times 10^{-14}
$$

Solve...
Let ' $x$ ' equal the change in concentration of hydronium ion...

$$
\begin{aligned}
(x)(x) & =1 \times 10^{-4} \\
x^{2} & =1 \times 10^{-14} \\
x & =1 \times 10^{-7} \mathrm{M}=\left[\mathrm{H}_{3} 0^{+}\right]=\left[0 H^{-}\right]
\end{aligned}
$$

- "p" notation helps us deal with the very small numbers we encounter when working with acids, bases, and water.
- based on log base 10

On a calculator, use

$$
\text { "p" means }-\log _{10}
$$

So,

$$
\begin{aligned}
& \rho H=-\log _{10}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-\mathrm{pH}} \\
& \rho \mathrm{OH}=-\log _{10}\left[\mathrm{OH}^{-}\right]\left[\left[\mathrm{OH}^{-}\right]=10^{-\mathrm{pOH}}\right.
\end{aligned}
$$

- Apply "p" notation to the water self-ionization reaction!

$$
\begin{gathered}
K_{W}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=1.00 \times 10^{-14} \\
\text { becomes } \ldots \\
K_{w}=p H+p O H=14.00
\end{gathered}
$$

Taking the " p " (negative log base ten) of the equilibrium constant is often used for BUFFER SOLUTIONS, which we'll discuss later!

ACIDITY AND ALKALINITY

- At $\mathrm{pH}=7, \mathrm{pH}=\mathrm{pOH}$. The solution is considered NEUTRAL

$$
\text { L Also, }\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right]!
$$

- At $\mathrm{pH}<7, \underline{\mathrm{pH}}<\mathrm{pOH}$. The solution is considered ACIDIC

$$
\text { L Also, }\left[\mathrm{H}^{+}\right]>\left[\mathrm{OH}^{-}\right]!
$$

- At pH $>7, \underline{\mathrm{pH}}>\mathrm{pOH}$. The solution is considered ALKALINE (BASIC)

$$
L \text { Also, }\left[\mathrm{H}^{+}\right]<\left[\mathrm{OH}^{-}\right]!
$$

The pH scale...

$$
\begin{aligned}
& \left|\begin{array}{c|}
\text { ACIDIC } \\
{\left[\mathrm{H}^{+}\right]>1 \times 10^{-7}}
\end{array} \frac{\text { ALKALINE }}{\left[\mathrm{H}^{+}\right]<1 \times 10^{-7}}\right| \\
& \mathrm{pH}=0 \\
& \mathrm{pH}=7 \\
& \mathrm{pH}=14 \\
& \text { NEUTRAL } \\
& {\left[\mathrm{H}^{+}\right]=1 \times 10^{-7}}
\end{aligned}
$$

pH AND TEMPERATURE

$$
p K_{w}=p H+p O H=14.00
$$

This equation is valid at room temperature, specifically $25^{\circ} \mathrm{C}$.
Equilibrium constants depend on TEMPERATURE, and change with temperature.
So, the "neutral" pH (where the concentration of hydroxide and hydronium ions are equal) CHANGES with changing temperatures

This change is important at temperatures greatly different from $25^{\circ} \mathrm{C}$.
As an example, consider average "normal" human body temperature: $37^{\circ} \mathrm{C}$

$$
\begin{array}{ll}
\text { At } 37^{\circ} \mathrm{C}, & \text { ptrw }=13.60 \\
& \text { pH of neutral solution }=6.8
\end{array}
$$

ACID-BASE EQUILIBRIUM IN WATER

- Like other ELECTROLYTES, acids and bases IONIZE to some extent in water
- STRONG electrolytes ionize completely. Acids and bases that ionize completely in water are called STRONG ACIDS and STRONG BASES
- WEAK electrolytes ionize partially, remaining mostly non-ionized. Acids and bases that ionize only partially in solution are called WEAK ACIDS and WEAK BASES.
- Most acids and bases are WEAK!

Common strong acids
HCl
$\mathrm{HNO}_{3}$
$\mathrm{H}_{2} \mathrm{SO}_{4}$ (only د $^{\text {st proton) }}$
HBr HI

Common strong bases

$$
\left.\begin{array}{l}
\mathrm{NaOH} \\
\mathrm{KOH}
\end{array}\right] \begin{aligned}
& \text { alhalimetal } \\
& \text { hydroxides } \\
& \text { (GroupIA) }
\end{aligned}
$$

- With strong acids and bases, the acid or base completely ionizes in water. So, we only have to worry about the effect of the acid or base on the water equilibrium itself.
- Since the equilibrium constant for the self-ionization of water is so small, the strong acid or base will. overpower the hydronium (for acids) or hydroxide (for bases) produced by the water.

$$
\mathrm{H}_{2} \mathrm{O}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} ; \mathrm{k}_{w}=1.0 \times 10^{-14}
$$

Consider a solution of 0.025 M nitric acid (a strong acid):

$$
\mathrm{HNO}_{3}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{NO}_{3}^{-}
$$

Assume that all hydronium ion in solution comes from the nitric acid, since the presence of the acid should suppress the self-ionization of water.

$$
\begin{aligned}
& \text { So, }\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{HWO}_{3}\right]_{\text {nominal }}= \\
& \rho H=-\log _{10}(0.025)=1.60
\end{aligned}
$$

$0.025 \mathrm{M} \mathrm{HzO}^{+}$

* For logarithms, the significant digits are BEHIND the decimal point. The numbers in front of the decimal represent the
What would the HYDROXIDE concentration be EXPONENT of the original number, and are not significant.

$$
\begin{aligned}
& \text { under these conditions? }\left[\begin{array}{l}
\left.\left[430^{+}\right][04]^{-}\right]=1.0 \times 10^{-14} \\
(0.025)[041]=1.0 \times 10^{-14} \\
{\left[041^{-}\right]=4.0 \times 10^{-13} \mathrm{M}}
\end{array}\right.
\end{aligned}
$$

... this also equals the concentration of HYDRONIUM PRODUCED BY WATER ITSELF, and it's really small compared to the 0.025 M produced by the acid!

Consider a solution of 0.0125 M sodium hydroxide (a strong base):

$$
\mathrm{NaOH}\left(\mathrm{naq}_{\mathrm{a}}\right) \rightarrow \mathrm{Na}^{t}\left(a_{q}\right)+\mathrm{OH}^{-}\left(\mathrm{aqq}_{\mathrm{q}}\right)
$$

Like the first example, we'll make an assumption. This time, we assume all the HYDROXIDE ION in solution comes from the NaOH . We expect the hydroxide ion production from water to be suppressed.

$$
\left[\mathrm{OH}^{-}\right]=\left[\mathrm{NHOH}_{\text {nominal }}=0.0125 \mathrm{MOH}^{-}\right.
$$

Wed like to know the pH ... First, find pOH

$$
P 04=-\log _{10}(0.0125)=1.90
$$

... then use the pH identities to find pH

$$
\begin{aligned}
& \text { PH }+\mathrm{POH}=14.00 \\
& \mathrm{PH}+1.90=14.00 \\
& p H=12.10
\end{aligned}
$$

Let's check the concentration of HYDRONIUM ION, since that will equal the amount of water that ionizes under these conditions. (We assumed this amount was very small compared to 0.0125 M ...)

$$
\begin{aligned}
{\left[H 3 O^{+}\right] } & =10^{-p H}=10^{-12.1} \\
{\left[H_{3} 0^{+}\right] } & =8.0 \times 10^{-13} \mathrm{M}
\end{aligned}
$$

Since this number also equals the amount of hydroxide produced by water itself, we can see that this number is ignorable small compared to 0.0125 M .

