## Equilibrium of Water



## Outcomes:

- Discuss the hydronium and hydroxide concentrations in water. Include the ion product of water.
- Given and one of the values $\mathrm{pH},\left[\mathrm{H}_{3} \mathrm{O}^{+}\right],\left[\mathrm{OH}^{-}\right]$, find the remaining values.


## Equilibrium of Water:

## Self-Ionization (Autoionization) of Water:

- Experiments have shown that PURE WATER can CONDUCT electricity VERY SLIGHTLY.
- Water can act as a PROTON DONOR and ACCEPTOR for ITSELF.
- When a PROTON is TRANSFERRED from one water molecule to another, the result is $\underline{\mathrm{H}}_{3} \mathbf{O}^{+}$and $\underline{\mathrm{OH}}^{-}$
i.e.)


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

This equilibrium can also be written as:

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

## Equilibrium of Water:

- In the above equilibrium, water acts as BOTH an ACID and a BASE $\rightarrow$ AMPHOTERIC
- Very few water molecule swill AUTOIONIZE (2 in 1 billion).
- The water equilibrium will obey the LAW of MASS ACTION, so:

$$
K_{\text {eq }}=\frac{\left[H_{(a q)}^{+}\right]\left[\mathrm{OH}_{(a q)}^{-}\right]}{\left[H_{2} O_{(l)}\right]}
$$

- Recall that LIQUIDS do NOT appear in an equilibrium law, so:

$$
K_{\mathrm{aq}}=\left[H_{(a q)}^{+}\right]\left[O H_{(a q)}^{-}\right]
$$

- It has been determined that at $25^{\circ} \mathrm{C},\left[\mathrm{H}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$are $\underline{1 \times 10^{-7} \mathrm{M}}$. Therefore,

$$
K_{e q}=\left[1 \times 10^{-7}\right]\left[1 \times 10^{-7}\right] \neq 1.0 \times 10^{-14}
$$

- This value is called the ION PRODUCT CONSTANT for WATER (Kw)


## Kw \& Temperature:

Note: $\underline{\mathbf{K}}_{\underline{\mathbf{w}}}$ will change with TEMPERATURE!

## Effect of Temperature on $\mathrm{K}_{\underline{w}}$

$$
\mathrm{H}_{2} \mathrm{O}_{(l)}+56.4 \mathrm{~kJ} \longleftrightarrow \mathrm{H}_{(a q)}^{+}+\mathrm{OH}_{(a q)}^{-}
$$

- If we increase the TEMPERATURE $\rightarrow$ reaction shifts RIGHT to reduce excess HEAT.
- $\left[\mathrm{H}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$will increase
antof $\left[\mathrm{H}_{2} \mathrm{O}\right]$ will decrease
- If we increase temperature to $60^{\circ} \mathrm{C},\left[\mathrm{H}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$become $3.0 \times 10^{-2} \mathrm{M}$, therefore:

$$
K_{W}=\left[3.0 \times 10^{-2}\right]\left[3.0 \times 10^{-2}\right]=9.55 \times 10^{-4}
$$

## Note:

$\rightarrow$ Always assume temperature is $25^{\circ} \mathrm{C}$, unless otherwise told, so $K_{w}=1.0 \times 10^{-14}$

## Not all solutions are neutral:

Le Chatelier's Principle applies to acidic/basic solutions... Addition of $\left[\mathrm{H}^{+}\right]$or $\left[\mathrm{OH}^{-}\right]$will SHIFT the equilibrium, DECREASING the concentration of the OTHER ION.

- i.e. If $\left[\mathrm{H}^{+}\right]$increases, $\left[\mathrm{OH}^{-}\right]$will decrease (and vice versa)

1. Neutral Solutions:

-     - [ $\left.\mathrm{H}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$are equal, ( $1 \times 10^{-7} \mathrm{M}$ )

2. Acidic Solutions:

- $\left[\mathrm{H}^{+}\right]$is greater than $\left[\mathrm{OH}^{-}\right]$( [ $\left.\left.\mathrm{H}^{+}\right]>1.0 \times 10^{-7} \mathrm{M}\right)$
- What would happen to $\left[\mathrm{H}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$if HCl is added to water?


$$
\begin{aligned}
& \mathrm{H}_{2} \mathrm{O}_{(l)} \longleftrightarrow \mathrm{H}_{(a q)}^{+}+\mathrm{OH}_{(a q)}^{-} \\
& \mathrm{HCl}_{(g)} \longleftrightarrow \mathrm{H}_{(a q)}^{+}+\mathrm{Cl}_{(a q)}^{-}
\end{aligned}
$$

$\rightarrow\left[\mathrm{H}^{+}\right]$increases (shifts to the left), so [ $\left.\mathrm{OH}^{-}\right]$decreases. Therefore pH will decrease.

## Not all solutions are neutral:

3. Basic Solutions:

- $\left[\mathrm{OH}^{-}\right]$is greater than $\left[\mathrm{H}^{+}\right]$. ([ $\left.\mathrm{OH}^{-}\right]>1.0 \times 10^{-7} \mathrm{M}$ )
- What would happen to $\left[\mathrm{H}^{+}\right]$and $\left[\mathrm{OH}^{-}\right]$if NaOH is added to water?


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

$\mathrm{NaOH}_{(g)} \longleftrightarrow \mathrm{Na}_{(a q)}+\mathrm{OH}_{(a q)}^{-}$
$\rightarrow\left[\mathrm{OH}^{-}\right]$increases (shifts to the left), so $\left[\mathrm{H}^{+}\right]$decreases. Therefore pH will increase.

- If we know the concentration of either $\left[\mathrm{H}^{+}\right]$or $\left[\mathrm{OH}^{-}\right]$, we can use the mass action expression and $\mathrm{K}_{\mathrm{w}}$ to find the other concentration.
- We can use these concentrations to determine whether a solution is acidic or basic.

> If,

$$
\begin{aligned}
& {\left[\mathrm{H}^{+}\right]>1.0 \times 10^{-7} \mathrm{M} \rightarrow \text { Acidic }} \\
& {\left[\mathrm{OH}^{-}\right]>1.0 \times 10^{-7} \mathrm{M} \rightarrow \text { Basic }}
\end{aligned}
$$

Example:
If $\left.\mathrm{H}^{+}\right]=1.0 \times 10^{-5} \mathrm{M}$, find the $\left[\mathrm{OH}^{-}\right]$and determine whether the solution is acidic, basic, or neutral.

Sol

$$
\begin{aligned}
K_{w} & =\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right] \\
1 \times 10^{-14} & =\left(1 \times 10^{-5}\right)\left[\mathrm{OH}^{-}\right] \\
{\left[\mathrm{OH}^{-}\right] } & =1 \times 10^{-9} \frac{\mathrm{mal}_{2}}{\mathrm{~L}}
\end{aligned}
$$

$\therefore$ Solution is acidic $\left[\mathrm{H}^{+}\right]>\left[\mathrm{OH}^{-}\right]$

$$
\left[\mathrm{H}^{+}\right]>1 \times 10^{-7} \frac{\mathrm{~mol}}{\mathrm{~L}}
$$

Try these ones:

1. If the $\left[\mathrm{OH}^{-}\right]$is $1.0 \times 10^{-3} \mathrm{M}$, what is the $\left[\mathrm{H}^{+}\right]$in the solution, and determine whether the solution is acidic, basic, or neutral.

$$
\begin{array}{ll}
K_{w}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right] \\
1 \times 10^{-14}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left(1 \times 1 \mathrm{O}^{-3}\right) & \therefore \text { Bosic } \\
{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1 \times 10^{-11} \frac{\mathrm{~mol}_{0}}{\mathrm{~L}}} & \left.\left[\mathrm{OH}^{-}\right]>\mathrm{H}_{3} \mathrm{O}^{+}\right]
\end{array}
$$

2. What is the $\left[\mathrm{H}^{+}\right]$in a solution of 0.030 MNaOH ? Determine whether the solution is acidic or basic.

$$
\begin{aligned}
& \begin{array}{l}
\mathrm{Mg}(\mathrm{OH})_{2} \\
0.03 \frac{\mathrm{~mol}}{\mathrm{~L}}
\end{array} \rightarrow \mathrm{Mg}^{2+}+\begin{array}{c}
204^{-} \\
0.06 \frac{\mathrm{mbl}}{\mathrm{~L}}
\end{array} \\
& k \omega_{\omega}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right] \\
& \times 10^{-14}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right](0.06) \\
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=1.67 \times 10^{-13} \frac{\mathrm{~mol}}{\mathrm{~L}}}
\end{aligned}
$$

$\therefore$ Sol is Basic

