ACIDS AND BASES
2: IONIZATION OF WATER, pH CALCULATION

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IONIZATION OF WATER

If we look at self-ionization of water, where water is the acid and the base, then we get the reaction below.

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

Base Acid Conj. Acid Conj. base

We can write the equilibrium expression as: $K_c = [H_3O^+][OH^-]$
(*Remember that liquids are not part of Kc expression*).

We call the equilibrium constant the ion-product constant, K_w.

$$\boxed{K_w = [H_3O^+][OH^-]}$$

At 25°C, $K_w = 1.0 \times 10^{-14}$ as shown by using the concentration of both hydronium and hydroxide ions as 1×10^{-7} M.

$$K_w = [1 \times 10^{-7}][1 \times 10^{-7}]$$

IMPLICATION OF K_W

K_w is calculated as follows: $\boxed{K_w = [H_3O^+][OH^-]}$

$1.0 \times 10^{-14} = [1 \times 10^{-7}][1 \times 10^{-7}]$

Solutions can be characterized as

Acidic when $[H_3O^+] > 1.0 \times 10^{-7}\ M$

Neutral when $[H_3O^+] = 1.0 \times 10^{-7}\ M$

Basic when $[H_3O^+] < 1.0 \times 10^{-7}\ M$

EXAMPLE 1: CALCULATION OF CONCENTRATIONS

Calculate the concentrations at 25°C in

a) Hydronium ions in 0.10 *M* HCl.

b) Hydroxide ions in 1.4×10^{-4} *M* $Mg(OH)_2$.

c) Hydroxide ions in 2.30×10^{-7} M nitric acid.

Answer:

a) When HCl ionizes, it gives H^+ and Cl^-.
So $[H^+] = [Cl^-] = [HCl] = \boxed{0.10\ M}$

b) When $Mg(OH)_2$ ionizes, it gives Mg^{2+} and 2 OH^-.
So $2[OH^-] = 2(1.4 \times 10^{-4}\ M) = \boxed{2.8 \times 10^{-4}\ M}$

c) Nitric acid dissociates completely. So $[H_3O^+]$ is 2.30×10^{-7} M. Use the K_w equation to find $[OH^-]$.

$$1.0 \times 10^{-14} = [H_3O^+][OH^-]$$

$$[OH^-] = 1.0 \times 10^{-14} / 2.30\times10^{-7} = \boxed{4.3\times10^{-8}\ M}$$

CALCULATING pH

$$\boxed{pH = -\log [H_3O^+]}$$

And inverse: $[H_3O^+] = 10^{-pH}$

- When pH = 7, the solution is neutral ($[H_3O^+] = 1.0 \times 10^{-7}$ *M*).
- When pH < 7.00, the solution is acidic ($[H_3O^+] > 1.0 \times 10^{-7}$ *M*).
- When pH > 7.00, the solution is basic ($[H_3O^+] < 1.0 \times 10^{-7}$ *M*).

Fluid	pH	Fluid	pH
Stomach acid	1.0	Saliva	6.4-6.9
Lemon juice	2.0	Milk	6.5
Vinegar	3.0	Pure water	7.0
Grapefruit juice	3.2	Blood	7.40
Orange juice	3.5	Milk of magnesia	10.6
Rain water	5.5	Household ammonia	11.5

$[H_3O^+]$ (M)	$-\log [H_3O^+]$	pH
0.10	$-\log (1.0 \times 10^{-1})$	1.00
0.010	$-\log (1.0 \times 10^{-2})$	2.00
1.0×10^{-3}	$-\log (1.0 \times 10^{-3})$	3.00
1.0×10^{-4}	$-\log (1.0 \times 10^{-4})$	4.00
1.0×10^{-5}	$-\log (1.0 \times 10^{-5})$	5.00
1.0×10^{-6}	$-\log (1.0 \times 10^{-6})$	6.00
1.0×10^{-7}	$-\log (1.0 \times 10^{-7})$	7.00
1.0×10^{-8}	$-\log (1.0 \times 10^{-8})$	8.00
1.0×10^{-9}	$-\log (1.0 \times 10^{-9})$	9.00
1.0×10^{-10}	$-\log (1.0 \times 10^{-10})$	10.00
1.0×10^{-11}	$-\log (1.0 \times 10^{-11})$	11.00
1.0×10^{-12}	$-\log (1.0 \times 10^{-12})$	12.00
1.0×10^{-13}	$-\log (1.0 \times 10^{-13})$	13.00
1.0×10^{-14}	$-\log (1.0 \times 10^{-14})$	14.00

EXAMPLE 2: CALCULATING pH

1) What is the pH of a solution that has a hydronium ion concentration of $6.5 \times 10^{-5} M$?

$$\boxed{pH = -\log [H_3O^+]}$$

$$pH = -\log [6.54 \times 10^{-5}]$$

$$\boxed{pH = 4.19}$$

2) What is the hydronium ion concentration of a solution with pH 3.65?

$$\boxed{[H_3O^+] = 10^{-pH}}$$

$$[H_3O^+] = 10^{-3.65}$$

$$\boxed{[H_3O^+] = 2.2 \times 10^{-4}\ M}$$

3) What is the pH of a 0.0570 M solution of HBr?

HBr ionizes completely so the conc. of the acid can be used as H_3O^+.

$$HBr(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Br^-(aq)$$

$$\boxed{pH = -\log [H_3O^+]}$$

$$pH = -\log[0.057]$$

$$\boxed{pH = 1.24}$$

pH ,pOH AND K_W

- pOH can be calculated just like pH.

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

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}}$$

- K_W is the hydronium ion and hydroxide ion concentrations; so pK_W is the addition of pH and pOH.

$$\boxed{K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}]}$$

$$\boxed{\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} = 14.00}$$

- Next slide has all relationships…

$$\begin{tikzcd}[column sep=huge, row sep=huge]
{[H_3O^+]} \arrow[r, shift left, "{[OH^-] = \frac{1 \times 10^{-14}}{[H_3O^+]}}"] \arrow[d, shift left, "{pH = -\log[H_3O^+]}"] & {[OH^-]} \arrow[l, shift left, "{[H_3O^+] = \frac{1 \times 10^{-14}}{[OH^-]}}"] \arrow[d, shift left, "{pOH = -\log[OH^-]}"] \\
pH \arrow[u, shift left, "{[H_3O^+\,] = 10^{-pH}}"] \arrow[r, shift left, "{pOH = 14 - pH}"] & pOH \arrow[u, shift left, "{[OH-] = 10^{-pOH}}"] \arrow[l, shift left, "{pH = 14 - pOH}"]
\end{tikzcd}$$

EXAMPLE 3: pOH CALCULATION

1) What is the pOH of a solution that has a hydroxide ion concentration of $4.3 \times 10^{-2} M$?

Answer: $\boxed{\mathrm{pOH} = -\log\,[\mathrm{OH}^-]}$ $\mathrm{pOH} = -\log\,[4.3 \times 10^{-2}]$

$\boxed{\mathrm{pOH} = 1.37}$

2) What is the hydroxide ion concentration of a solution with pH 8.35?

Answer: $\boxed{[\mathrm{H}^+] = 10^{-pH}}$ $[\mathrm{H}^+] = 10^{-8.35}$

$[\mathrm{H}^+] = 4.5 \times 10^{-9}$

$\boxed{K_w = [H_3O^+][OH^-]}$ $1.0 \times 10^{-14} = 4.5 \times 10^{-9}\,[\mathrm{OH}^-]$

$[\mathrm{OH}^-] = 1.0 \times 10^{-14}/4.5 \times 10^{-9} = \boxed{2.22 \times 10^{-6}\ \mathrm{M}}$

<u>2nd way:</u>

$\mathrm{pOH} = 14 - 8.35 = 5.65$

Now use: $\boxed{[\mathrm{OH}^-] = 10^{-pOH}}$

EXAMPLE 4: CALCULATING pH OF BASES

What is the pH of a solution of 0.0340 M solution of $Ca(OH)_2$?

Answer:

$Ca(OH)_2$ ionizes to give 2 mols of OH^-, so conc. has to be doubled.

$$Ca(OH)_{2\,(aq)} \longrightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

$$[OH^-] = 0.034M\ Ca(OH)_2 \times \frac{2\text{ mol }OH^-}{1\text{ mol }Ca(OH)_2}$$

$$\boxed{pOH = -\log[OH^-]}$$

$$[OH^-] = 0.068M$$

$$pOH = -\log[0.068] = 1.17$$

$$pH = 14 - pOH$$
$$= 14 - 1.17 = \boxed{12.8}$$

STRONG ACIDS AND BASES

- All strong acids and bases ionize completely; so their concentrations can be used to calculate the pH and pOH.
- For diprotic acids, e.g. sulfuric acid only the first ionization reactions is measured; on the contrary dihydroxide bases will ionize to give two hydroxides in solution.

Strong Acid	Ionization Reaction
Hydrochloric acid	$HCl_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$
Hydrobromic acid	$HBr_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + Br^-_{(aq)}$
Hydroiodic acid	$HI_{(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + I^-_{(aq)}$
Nitric acid	$HNO_{3\,(aq)} + H_2O_{(l)} \longrightarrow H_3O_{(aq)} + NO_3^-{}_{(aq)}$
Perchloric acid	$HClO_{4\,(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + ClO_4^-{}_{(aq)}$
Sulfuric acid	$H_2SO_{4\,(aq)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + HSO_4^-{}_{(aq)}$

Group 1 Hydroxides	Group II hydroxides
$LiOH_{(aq)} \longrightarrow Li^+_{(aq)} + OH^-_{(aq)}$	$Ca(OH)_{2(s)} \longrightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$
$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$	$Ba(OH)_{2(s)} \longrightarrow Ba^{2+}_{(aq)} + 2OH^-_{(aq)}$

KEY CONCEPTS

- Calculation of pH and pOH
- Calculation of hydronium and hydroxide ion conc.