MOLECULAR STRUCTURE AND ACID STRENGTH

- The strength of an acid depends on how easily a H^+ is removed from the H – X bond.
- Ease of H^+ loss is determined by 2 factors

1. The Polarity of the H – X bond
   - The polarity of the H – X bond depends on the ΔEN (electronegativity difference) between the atoms involved in the bond

The higher the E.N. of X → The higher the ΔEN → The more polar the bond → The easier to lose the H^+ → The stronger the acid

2. The strength of the H – X bond
   - The strength of the H – X bond depends on the size of X (smaller atoms form stronger bonds)

The larger X is → The weaker the H – X bond → The less tightly the H is held → The easier to lose the H^+ → The stronger the acid

Trends among Binary Acids (HX)

- Recall that binary acids do not contain O atoms

1. Across a period going from left to right
   - The polarity of the H — X bond determines this trend.

Electronegativity of X increases →

➢ Polarity of the H — X increases

Consequently:

➢ H_2O is a weaker acid than HF $H_2O < HF$

➢ H_2S is a weaker acid than HCl $H_2S < HCl$

2. Going down a group
   - The strength of the H – X bond determines this trend

F	Atomic Size Increases (more electron shells) ↓	H – F	Strength of Bond Decreases ↓	Acidic Strength Increases ↓
Cl		H – Cl		
Br		H – Br		
I		H – I		

Trends among Oxoacids

- Oxoacids are O containing acids

δ+ δ–
H — O — Y

acidic H is always attached to an O atom

- The polarity of the H — O bond determines the relative acidic strength
- The polarity of the H — O bond depends on 2 factors:

1. The Electronegativity of the Y atom

The more electronegative Y is ➡ The more polar the H — O bond ➡ The easier to lose the H^+ ➡ The stronger the acid

$EN_{(Cl)} = 3.16$		$EN_{(Br)} = 2.96$		$EN_{(I)} = 2.66$
H – O – Cl hypochlorous acid **(strongest)**	>	H – O – Br hypobromos acid	>	H – O – I hypoiodos acid **(weakest)**

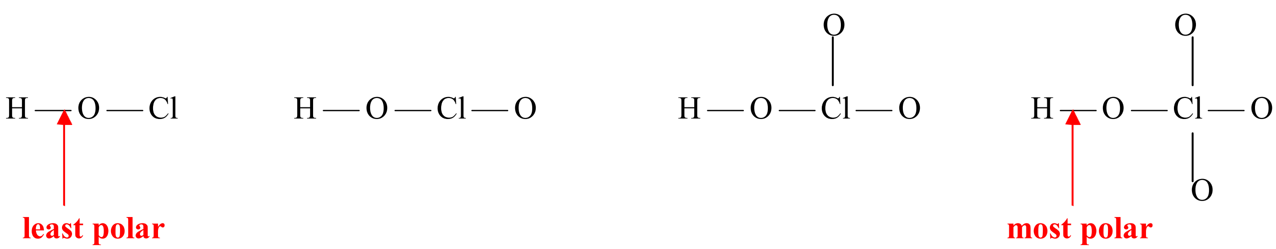
ACIDIC STRENGTH INCREASES ←

2. The number of O atoms bonded to Y (excluding O in OH groups)

The more O atoms bonded to Y ➡ The more electronegative Y becomes ➡ The more polar the H — O — Y bond becomes ➡ The stronger the acid

HClO hypochlorous acid **(weakest)**	<	$HClO_2$ chlorous acid	<	$HClO_3$ chloric acid	<	$HClO_4$ perchloric acid **(strongest)**

ACIDIC STRENGTH INCREASES →



SUMMARY

- BINARY ACIDS (no O)

Acidic Strength Increases

(H – X polarity increases)

Acidic Strength Increases (H – X bond weakens) (size of X increases)

- OXOACIDS (H attached to Y through O)

Acidic Strength Increases (Polarity of H – O increases)

The more O atoms attached to Y, the stronger the acid

- POLYPROTIC ACIDS
  - contain more than one acidic H
  - are stronger than their corresponding anions

H_2SO_4 > HSO_4^-

strong acid   weak acid

H_3PO_4 > $H_2PO_4^-$ > HPO_4^{2-}

Acidic Strength Increases

Reason: The acid strength of a polyprotic acid and its anion(s) decreases with increasing negative charge (it becomes increasingly difficult to lose a H^+)

SELF-IONIZATION OF WATER

- Pure Water is generally considered a non-electrolyte.
- It is actually a very, very weak electrolyte:

$$H_2O\,(l) + \overset{H^+}{H_2O\,(l)} \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

$$\mathbf{K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}}$$

- K_c is very small
- The equilibrium is strongly shifted to the left

- $[H_2O]^2$ = is essentially constant
- $[H_2O]$ for 1L of water can be calculated as follows:

$$?\frac{\text{moles}}{\text{L}} = 1\text{ L} \times \frac{1000\text{ g}}{1\text{ L}} \times \frac{1\text{ mole}}{18.02\text{ g}} \approx 55\text{ M}$$

- $[H_2O]^2 \times K_c = [H_3O^+]\,[OH^-] =$ **$K_w = 1.0 \times 10^{-14}$**

  K_w = is called THE ION-PRODUCT OF WATER

  = 1.0×10^{-14} at 25^0C (is temperature dependent)

- **CONCLUSION: $K_w = [H_3O^+]\,[OH^-] = 1.0 \times 10^{-14}$ (25^0C)**

In Pure Water: $[H_3O^+] = [OH^-] = x$

$K_w = x^2$ $\qquad x = \sqrt{K_w} = \sqrt{1.0\times10^{-14}}$

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

Solution of a Strong Acid:

Example: A 0.1 M solution of HCl

$$\begin{array}{lcccc} HCl\,(aq) & + & H_2O\,(l) & \xrightarrow[\text{ionization}]{\text{complete}} & H_3O^+\,(aq) & + & Cl^-\,(aq) \\ 0 & & & & 0.1\text{ M} & & 0.1\text{ M} \end{array}$$

- The TOTAL CONCENTRATION OF THE $[H_3O^+]$ can be thought of as the sum of the:

  - concentration of $[H_3O^+]$ provided by the acid; $[H_3O^+] = 1.0 \times 10^{-1}$ M
  - concentration of $[H_3O^+]$ provided by the self-ionization of water; $[H_3O^+] = 1.0 \times 10^{-7}$ M

Actually, this is even less than that. Reason:

- According to **Le Chatelier's principle**, the equilibrium of the self-ionization of water, is shifted to the left, by the presence of the excess $[H_3O^+]$ provided by the acid:

$$\mathbf{H_2O\,(l) \;+\; H_2O\,(l) \rightleftharpoons H_3O^+(aq) \;+\; OH^-\,(aq)}$$

Stress:			**H_3O^+(aq) added**	
Response:		$\longleftarrow$		
New Equil:	increased	increased	increased **but slightly**	decreased

Total Conc. of $[H_3O^+]$ = $[H_3O^+]$ from acid + $[H_3O^+]$ from self-ionization of water

= **1.0×10^{-1} M** + less than 1.0×10^{-7} M (negligible)

= **1.0×10^{-1} M**

- Concentration of the $[OH^-]$ can now easily be calculated:

$$[H_3O^+]\,[OH^-] = 1.0 \times 10^{-14} \qquad [OH] = \frac{1.0 \times 10^{-14}}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-1}} = 1.0 \times 10^{-13}\text{ M}$$

CONCLUSION:

- In a solution of a strong acid the concentration of the $[H_3O^+]$ produced by the self-ionization of water can be ignored.

- NOTE: The situation is different if the solution of the strong acid is very dilute:
  Example: HCl(aq) 1.0×10^{-7} M

TOTAL $[H_3O^+]$ = $[H_3O^+]$ from acid + $[H_3O^+]$ from water

= 1.0×10^{-7} M + 1.0×10^{-7} M (cannot be ignored)

= 2.0×10^{-7} M

In a solution of a Strong Base:

Example: A 0.010 M solution of NaOH

$$\text{NaOH (aq)} \xrightarrow[\text{ionization}]{\text{complete}} \text{Na}^+\text{(aq)} + \text{OH}^-\text{(aq)}$$

0		0.010 M	0.010 M

- The TOTAL CONCENTRATION OF THE $[OH^-]$ can be thought of as the sum of the :
  - concentration of $[OH^-]$ provided by the base; $[OH^-] = 1.0 \times 10^{-2}$ M
  - concentration of $[OH^-]$ provided by the self-ionization of water; $[OH^-] = 1.0 \times 10^{-7}$ M

Actually, this is even less than that. Reason:

- According to **Le Chatelier's principle**, the equilibrium of the self-ionization of water, is shifted to the left, by the presence of the excess $[OH^-]$ provided by the acid:

$$\mathbf{H_2O\ (l) + H_2O\ (l) \rightleftharpoons H_3O^+(aq) + OH^-\ (aq)}$$

Stress:				**OH^-(aq) added**
Response:		$\leftarrow$		
New Equil:	increased	increased	decreased	increased **but slightly**

Total Conc. of $[OH^-]$ = $[OH^-]$ from base + $[OH^-]$ from self-ionization of water

= **1.0×10^{-2} M** + less than 1.0×10^{-7} M (negligible)

= **1.0×10^{-2} M**

- Concentration of the $[H_3O^+]$ can now easily be calculated:

$$[H_3O^+][OH^-] = 1.0 \times 10^{-14} \qquad [H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}$$

CONCLUSION:

- In a solution of a strong base the concentration of the $[OH^-]$ produced by the self-ionization of water can be ignored.

- NOTE: The situation is different if the solution of the strong base is very dilute:

  Example: NaOH(aq) 1.0×10^{-7} M

  TOTAL $[OH^-]$ = $[OH^-]$ from base + $[OH^-]$ from water

  = 1.0×10^{-7} M + 1.0×10^{-7} M (cannot be ignored)

  = 2.0×10^{-7} M

CONCLUSIONS:

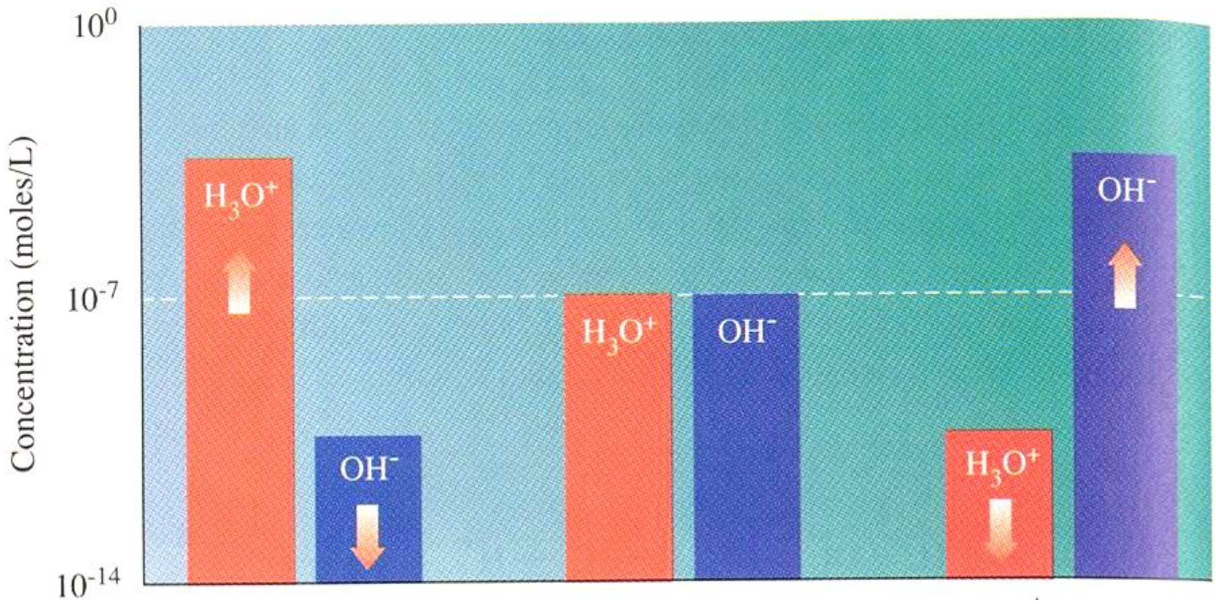
1. In a neutral solution: $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ M

2. In an acidic solution: $[H_3O^+] > [OH^-]$

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

2. In a basic solution: $[H_3O^+] < [OH^-]$

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



Examples:

1. What is the concentration of the $[H_3O^+]$ and $[OH^-]$ in a 0.25 M solution of $Ba(OH)_2$?

$$\begin{array}{llll} Ba(OH)_2\,(aq) & \longrightarrow\quad Ba^{2+}\,(aq) & + & 2OH^-\,(aq) \\ 0 & \qquad\quad 0.25\text{ M} & & 2 \times 0.25\text{ M} \end{array}$$

$[OH^-] = 0.50$ M

$[H_3O^+]$ =

2. What is the concentration of the $[H_3O^+]$ and $[OH^-]$ in a 0.040 M solution of HNO_3?

3. Identify each of the following solutions are acidic, basic or neutral:

   a) $[OH^-] = 1.0 \times 10^{-5}$ M

   b) $[H_3O^+] = 3.8 \times 10^{-9}$ M

   c) $[H_3O^+] = 6.2 \times 10^{-3}$ M

   d) $[OH^-] = 4.5 \times 10^{-10}$ M

pH SCALE

- pH is an important chemical quantity introduced by Sorensen, to simplify handling of negative exponents, when expressing the acidity or basicity of aqueous solutions
- pH can be loosely referred to as "power of hydrogen)
- By Sorensen's definition, widely accepted today:

$$pH = -\log [H_3O^+] \qquad \text{or simply:} \qquad pH = -\log [H^+]$$

  - For a neutral solution: $[H_3O^+] = 1.0 \times 10^{-7}$ M
    $pH = -\log (1.0 \times 10^{-7}) = 7.00$
  - **For an acidic solution: $[H_3O^+] > 1.0 \times 10^{-7}$ M**
    $pH < 7.00$
  - **For a basic solution: $[H_3O^+] < 1.0 \times 10^{-7}$ M**
    $pH > 7$

- pH calculations can be greatly simplified by a rearrangement of the expression:

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

Taking logs of both sides:

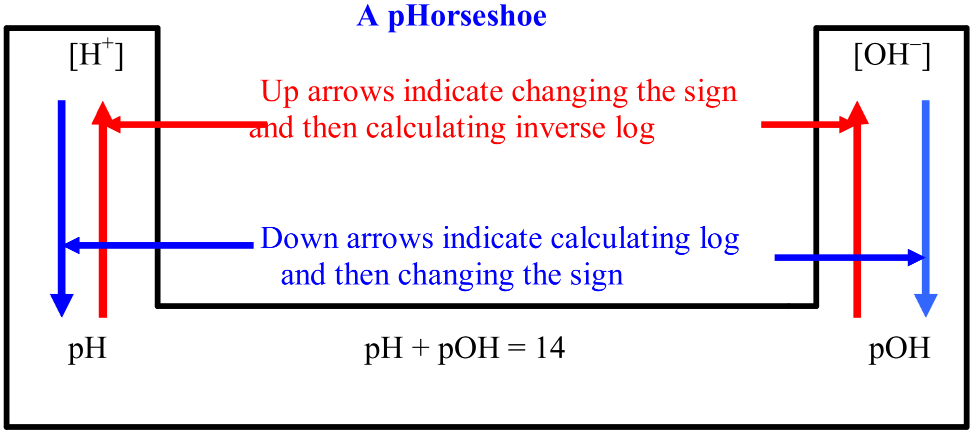
$$\log [H_3O^+] + \log [OH^-] = \log (1.0 \times 10^{-14})$$

$$-pH \;-\; pOH \;=\; -14.00$$

$$\boxed{pH + pOH = 14.00}$$

- NOTE: $pOH = -(\log [OH^-])$

A pHorseshoe



Examples:

1. Obtain the pH corresponding to a hydroxide-ion concentration of 2.7×10^{-10} M.

$$pOH = -\log(2.7 \times 10^{-10}) = 9.5\underline{6}8$$

$$pH = 14.00 - 9.5\underline{6}8 \quad = 4.43$$

2. A wine was tested for acidity, and it pH was found to be 3.85 at 25 °C. What is the hydronium ion concentration?

$$\log [H_3O^+] = -pH = -3.85$$

$$[H_3O^+] = \text{antilog}(-3.85) = 10^{-3.85} = 1.4 \times 10^{-4}\ M$$

3. A 1.00 L aqueous solution contains 6.78 g of $Ba(OH)_2$. What is the pH of the solution?

First: Calculate the molarity of the $Ba(OH)_2$ solution:

$$?\ \frac{\text{moles}}{\text{L}} = \frac{6.78\ g\ Ba(OH)_2}{1.00\ L\ \text{solution}} \times \frac{1 mol\ Ba(OH)_2}{171.4\ g\ Ba(OH)_2} = 0.039\underline{5}6\ M\ Ba(OH)_2$$

$$[OH^-] = 0.039\underline{5}6\ M\ Ba(OH)_2 \times \frac{2\ \text{moles}\ OH^-}{1\ \text{mole}\ Ba(OH)_2} = 0.079\underline{1}2\ M$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{0.079\underline{1}2\ M} = 1.\underline{2}64 \times 10^{-13}\ M$$

$$pH = -\log(\mathbf{1.\underline{2}}64 \times 10^{-13}\ M) = 12.\mathbf{90}$$

4. What is concentration of a solution of KOH with a pH of 11.89?

MEASUREMENT OF pH

Acid-Base Indicators

- Acid-Base indicators change color within a small range.
- Reason: Indicators establish an equilibrium between their acid form and their base form, respectively:

HIn = acid form of indicator
In^- = base form of indicator

- These two forms of the Indicator have different colors (not necessarily red and blue)

$$\mathbf{HIn\ (aq)} + H_2O\ (aq) \rightleftharpoons H_3O^+\ (aq) + \mathbf{In^-\ (aq)}$$

Example: Phenolphthalein: HIn (aq) is colorless **In^-(aq) is pink**

- When a base is added to the acidic solution of phenolphthalein:

$$HIn\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+(aq) + \mathbf{In^-(aq)}$$

  - OH^- reacts with H_3O^+(aq) to produce H_2O
  - Equilibrium shifts ——>
  - **In^-(aq)** is produced. Solution turns pink
  - Phenolphthalein begins to turn pink at about pH = 8.0

Universal pH paper

- This paper is impregnated with several indicators
- It gives different colors to different pH ranges (to the nearest integer value)

pH-meter

- Consists of two electrodes (or one combination electrode) dipped into the solution whose pH is to be measured.
- Measures the voltage that is generated between the electrodes.
- This voltage depends on pH and is read on a meter calibrated directly in pH units.