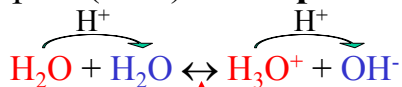


## 18.2 Autoionization of Water and pH

- Water can act as both proton donor (acid) and proton acceptor (base) → **amphoteric**



Autoionization (autoprotolysis)

- Ion-product constant** of water ( $K_w$ )

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \quad \rightarrow [\text{H}_2\text{O}] \text{ can be assumed constant and combined with } K_c$$

$$\Rightarrow K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \rightarrow K_w = K_c[\text{H}_2\text{O}]^2$$

$K_w$  → **ion-product** (autoprotolysis) constant of water

➤ At 25°C,  $K_w = 1.0 \times 10^{-14}$

➤ **In pure water** →  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = x$

$$\rightarrow K_w = x^2 \quad \rightarrow x = \sqrt{K_w} = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$$

$$\Rightarrow [\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

➤ **In water solutions** →  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  are inversely proportional to each other

$$\rightarrow K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \Rightarrow \uparrow[\text{H}_3\text{O}^+] \leftrightarrow \downarrow[\text{OH}^-]$$

⇒  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  are present in different proportions in both acid and base solutions

Neutral solutions →  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$

Acidic solution →  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$

Basic solutions →  $[\text{H}_3\text{O}^+] < [\text{OH}^-]$

**Example:** Calculate the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in 0.10 M HCl and 0.10 M  $\text{Ba}(\text{OH})_2$  solutions.

→ HCl is a strong acid → completely dissociated in water solutions;  $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$

$$\Rightarrow 0.10 \text{ M HCl} \rightarrow [\text{H}_3\text{O}^+] = 0.10 \text{ M}$$

$$\Rightarrow [\text{OH}^-] = K_w / [\text{H}_3\text{O}^+] = 1.0 \times 10^{-14} / 0.10$$

$$\Rightarrow [\text{OH}^-] = 1.0 \times 10^{-13} \text{ M} \quad \Rightarrow [\text{H}_3\text{O}^+] \gg [\text{OH}^-]$$

→  $\text{Ba}(\text{OH})_2$  is a strong base → completely dissociated in water solutions;  $\text{Ba}(\text{OH})_2 \rightarrow \text{Ba}^{2+} + 2\text{OH}^-$

$$\Rightarrow 0.10 \text{ M Ba}(\text{OH})_2 \rightarrow [\text{OH}^-] = 0.20 \text{ M}$$

$$\Rightarrow [\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = 1.0 \times 10^{-14} / 0.20$$

$$\Rightarrow [\text{H}_3\text{O}^+] = 5.0 \times 10^{-14} \text{ M} \quad \Rightarrow [\text{H}_3\text{O}^+] \ll [\text{OH}^-]$$

## The pH Scale

- The pH scale is a logarithmic scale

$$pH = -\log[\text{H}_3\text{O}^+]$$

$$\rightarrow \log[\text{H}_3\text{O}^+] = -pH \quad \Rightarrow [\text{H}_3\text{O}^+] = 10^{-pH}$$

$$\uparrow[\text{H}_3\text{O}^+] \leftrightarrow \downarrow pH$$

→ If  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}$  (neutral solution)

$$\rightarrow pH = -\log(1 \times 10^{-7}) \rightarrow \text{neutral solution} \rightarrow pH = 7$$

→ If  $[\text{H}_3\text{O}^+] > 1 \times 10^{-7} \text{ M}$  → acidic solution →  $pH < 7$

→ If  $[\text{H}_3\text{O}^+] < 1 \times 10^{-7} \text{ M}$  → basic solution →  $pH > 7$

**Examples:**  $[\text{H}_3\text{O}^+] = 1 \rightarrow pH = -\log 1 = 0$

$$[\text{H}_3\text{O}^+] = 10^{-14} \rightarrow pH = -\log 10^{-14} = 14$$

• The  $p$ -notation  $\rightarrow pX = -\log X$

$$pOH = -\log[OH^-]$$

$$\rightarrow \log[OH^-] = -pOH \Rightarrow [OH^-] = 10^{-pOH}$$

$$pK_w = -\log K_w$$

$$\rightarrow [H_3O^+][OH^-] = K_w \leftarrow (\text{take a } -\log)$$

$$\rightarrow -\log[H_3O^+] + (-\log[OH^-]) = -\log K_w$$

$$\Rightarrow pH + pOH = pK_w$$

$$\rightarrow \text{At } 25^\circ\text{C}, K_w = 1.0 \times 10^{-14} \rightarrow pK_w = 14.00$$

$$\Rightarrow pH + pOH = 14.00$$

$$\rightarrow \text{If } pH = 7 \rightarrow pOH = 7 \rightarrow \text{neutral solution}$$

$$\rightarrow \text{Acidic } (\downarrow pH, \uparrow pOH); \text{ Basic } (\uparrow pH, \downarrow pOH)$$

	$[H_3O^+]$	pH	$[OH^-]$	pOH
BASIC	$1.0 \times 10^{-15}$	15.00	$1.0 \times 10^1$	-1.00
	$1.0 \times 10^{-14}$	14.00	$1.0 \times 10^0$	0.00
	$1.0 \times 10^{-13}$	13.00	$1.0 \times 10^{-1}$	1.00
	$1.0 \times 10^{-12}$	12.00	$1.0 \times 10^{-2}$	2.00
	$1.0 \times 10^{-11}$	11.00	$1.0 \times 10^{-3}$	3.00
	$1.0 \times 10^{-10}$	10.00	$1.0 \times 10^{-4}$	4.00
	$1.0 \times 10^{-9}$	9.00	$1.0 \times 10^{-5}$	5.00
	$1.0 \times 10^{-8}$	8.00	$1.0 \times 10^{-6}$	6.00
NEUTRAL	$1.0 \times 10^{-7}$	7.00	$1.0 \times 10^{-7}$	7.00
ACIDIC	$1.0 \times 10^{-6}$	6.00	$1.0 \times 10^{-8}$	8.00
	$1.0 \times 10^{-5}$	5.00	$1.0 \times 10^{-9}$	9.00
	$1.0 \times 10^{-4}$	4.00	$1.0 \times 10^{-10}$	10.00
	$1.0 \times 10^{-3}$	3.00	$1.0 \times 10^{-11}$	11.00
	$1.0 \times 10^{-2}$	2.00	$1.0 \times 10^{-12}$	12.00
	$1.0 \times 10^{-1}$	1.00	$1.0 \times 10^{-13}$	13.00
	$1.0 \times 10^0$	0.00	$1.0 \times 10^{-14}$	14.00
	$1.0 \times 10^1$	-1.00	$1.0 \times 10^{-15}$	15.00

**Example:** A household ammonia solution has a  $pH$  of 11.92. What is the  $pOH$  and the concentration of  $OH^-$  in it?

$$\rightarrow pOH = 14.00 - pH = 14.00 - 11.92 = 2.08$$

$$\rightarrow [OH^-] = 10^{-pOH} = 10^{-2.08} = 8.3 \times 10^{-3}$$

**Note:** The # of sig. figs in  $[OH^-]$  (or  $[H_3O^+]$ ) equals the number of decimal places in  $pOH$  (or  $pH$ )

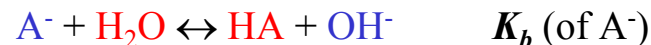
• **Measuring  $pH$  in the laboratory**

– **Indicators** – have different colors at different  $pH$  ( $pH$  paper, indicator solutions)

–  **$pH$  meters** – measure the  $pH$  by measuring the potential of a  $pH$  sensitive electrode immersed in the solution (more accurate)

### $K_a$ and $K_b$ of a Conjugate Acid-Base Pair

• In a solution of the weak acid  $HA$ , both  $HA$  and its conjugate base,  $A^-$ , react with water



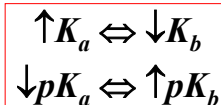
$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w$$

$$\Rightarrow \text{For a conjugate acid-base pair} \rightarrow K_a \times K_b = K_w$$

$$-\log K_a + (-\log K_b) = -\log K_w$$

$$\Rightarrow pK_a + pK_b = pK_w \rightarrow \text{At } 25^\circ\text{C}, pK_a + pK_b = 14.00$$

➤ The stronger the acid, the weaker its conjugate base and vice versa



**Example:** The  $K_a$  of HF is  $6.8 \times 10^{-4}$ . What is the  $K_b$  of  $F^-$ ?

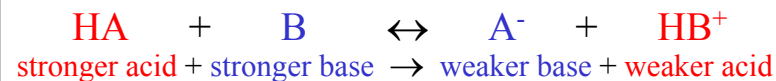
$$K_b = K_w / K_a = 1.0 \times 10^{-14} / 6.8 \times 10^{-4}$$

$$K_b = 1.5 \times 10^{-11}$$

ACID STRENGTH		BASE STRENGTH			
Strong	HCl	Cl <sup>-</sup>	Negligible		
	H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>			
	HNO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>			
	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O			
	Weak	HSO <sub>4</sub> <sup>-</sup>		SO <sub>4</sub> <sup>2-</sup>	Weak
		H <sub>2</sub> SO <sub>3</sub>		HSO <sub>3</sub> <sup>-</sup>	
		H <sub>3</sub> PO <sub>4</sub>		H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	
		HF		F <sup>-</sup>	
		CH <sub>3</sub> COOH		CH <sub>3</sub> COO <sup>-</sup>	
		H <sub>2</sub> CO <sub>3</sub>		HCO <sub>3</sub> <sup>-</sup>	
Negligible	H <sub>2</sub> S	HS <sup>-</sup>	Strong		
	HSO <sub>3</sub> <sup>-</sup>	SO <sub>3</sub> <sup>2-</sup>			
	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	HPO <sub>4</sub> <sup>2-</sup>			
	HCN	CN <sup>-</sup>			
	NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>			
	H <sub>2</sub> O	OH <sup>-</sup>			
	HS <sup>-</sup>	S <sup>2-</sup>			
	OH <sup>-</sup>	O <sup>2-</sup>			

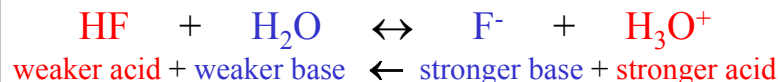
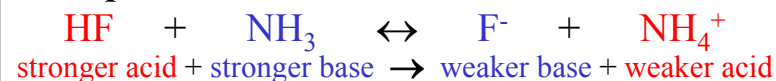
### 18.3 Relative Acid-Base Strength and the Net Direction of Reaction

- An acid-base reaction proceeds to a greater extent from the stronger acid and stronger base towards the weaker acid and weaker base



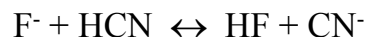
→ The reaction is shifted towards A<sup>-</sup> and HB<sup>+</sup> ( $K_c > 1$ )

**Examples:**



**Example:**

Given  $K_a(\text{HF}) = 6.8 \times 10^{-4}$  and  $K_a(\text{HCN}) = 6.2 \times 10^{-10}$ , determine the preferred direction of the reaction



→ Compare the strengths of the acids on both sides

→ HF is stronger than HCN (HF has higher  $K_a$  value)

→ Compare the strengths of the bases on both sides

→ Since HF is a stronger acid than HCN, the conjugate base of HF,  $F^-$ , is a weaker base than the conjugate base of HCN,  $CN^-$

→  $CN^-$  is stronger than  $F^-$  ( $CN^-$  has higher  $K_b$  value)

⇒  $\text{F}^- + \text{HCN} \Leftrightarrow \text{HF} + \text{CN}^-$  is shifted to the left ( $K_c < 1$ )