

## **Announcements – Lecture XIV – Tuesday, Mar 20<sup>th</sup>**

1. iClicker:



Pick any letter a-e

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2. Quiz 6:

Due in class on Thursday, March 22<sup>nd</sup>.

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3. Exam II:

Moved to Saturday, April 7<sup>th</sup>.

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## 16.2 Water and the pH Scale

### Autoionization of Water – Neutral/Acidic/Basic Solutions

A solution at **25°C** has a hydronium ion concentration of  **$4.5 \times 10^{-4} \text{ M}$** . This solution is:



- a) Acidic ✓
- b) Basic
- c) Neutral

$$[\text{H}_3\text{O}^+] = 4.5 \times 10^{-4}$$

$$[\text{H}_3\text{O}^+] [\text{OH}^-] = 1 \times 10^{-14} \text{ @ } 25^\circ\text{C}$$
$$(4.5 \times 10^{-4}) [\text{OH}^-] = 1 \times 10^{-14}$$

$$[\text{OH}^-] = \frac{1 \times 10^{-14}}{4.5 \times 10^{-4}}$$
$$= 2.2 \times 10^{-11}$$

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



## 16.2 Water and the pH Scale pH and pOH Calculations

In general :  $\rho X = -\log_{10} X$

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

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

@ 25°C :

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$$

$$\log_{10}([\text{H}_3\text{O}^+][\text{OH}^-]) = \log_{10}(1 \times 10^{-14})$$

$$\log_{10}[\text{H}_3\text{O}^+] + \log_{10}[\text{OH}^-] = -14$$

$$-\underbrace{\log_{10}[\text{H}_3\text{O}^+]}_{\text{pH}} - \underbrace{\log_{10}[\text{OH}^-]}_{\text{pOH}} = 14$$

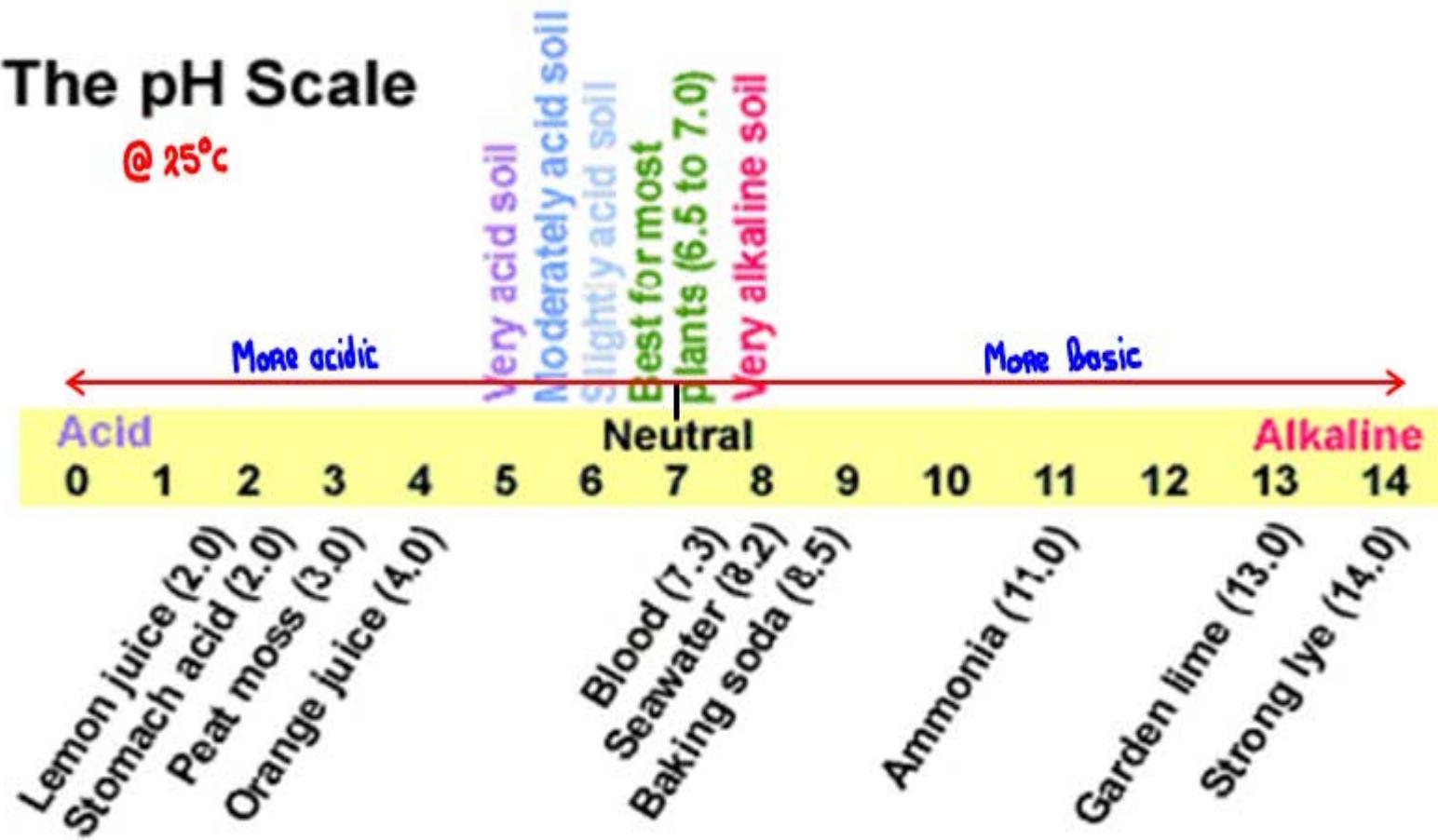
$$\text{pH} + \text{pOH} = 14 @ 25^\circ\text{C}$$

## 16.2 Water and the pH Scale

### Autoionization of Water – Neutral/Acidic/Basic Solutions

#### The pH Scale

@ 25°C



## 16.3 Acid and Base Strength

### Acid and Base Strength

#### Acid Ionization

Acid:

- H<sub>3</sub>PO<sub>4</sub>
- CH<sub>3</sub>CO<sub>2</sub>H
- H<sub>2</sub>CO<sub>3</sub>
- HCl
- HNO<sub>3</sub>
- HClO<sub>4</sub>

Ionize

See Class Web Site:

Six Strong Acids:



Six Strong Bases:



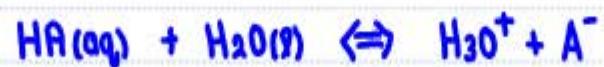
Ionized acid is indicated by red in the above diagram



## 16.3 Acid and Base Strength

### Acid and Base Hydrolysis Equilibria, $K_a$ , and $K_b$

WEAK ACIDS:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

WEAK BASES:



$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$



## 16.3 Acid and Base Strength

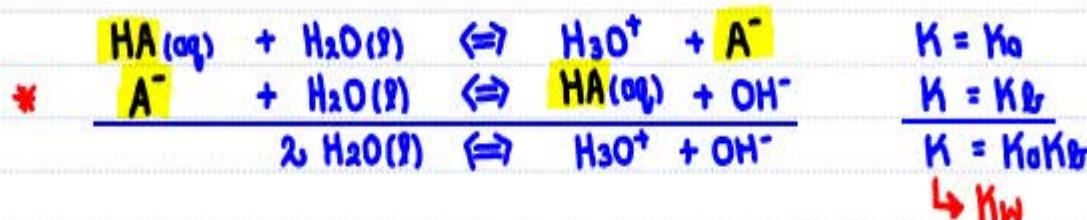
### Acid and Base Hydrolysis Equilibria, $K_a$ , and $K_b$

| $K_a$ Values          |                   |                      | $K_a$ Values             |                   |                       |
|-----------------------|-------------------|----------------------|--------------------------|-------------------|-----------------------|
| Name of Acid          | Acid              | $K_a$                | Name of Acid             | Acid              | $K_a$                 |
| Sulfuric acid         | $H_2SO_4$         | large                | Hexaaquaaluminum ion     | $Al(H_2O)_6^{3+}$ | $7.9 \times 10^{-6}$  |
| Hydrochloric acid     | HCl               | large                | Carbonic acid            | $H_2CO_3$         | $4.2 \times 10^{-7}$  |
| Nitric acid           | $HNO_3$           | large                | Hydrogen sulfide         | $H_2S$            | $1 \times 10^{-7}$    |
| Hydronium ion         | $H_3O^+$          | 1.0                  | Dihydrogen phosphate ion | $H_2PO_4^-$       | $6.2 \times 10^{-8}$  |
| Hydrogen sulfate ion  | $HSO_4^-$         | $1.2 \times 10^{-2}$ | Hypochlorous acid        | HCIO              | $3.5 \times 10^{-8}$  |
| Phosphoric acid       | $H_3PO_4$         | $7.5 \times 10^{-3}$ | Ammonium ion             | $NH_4^+$          | $5.6 \times 10^{-10}$ |
| Hexaaquairon(III) ion | $Fe(H_2O)_6^{3+}$ | $6.3 \times 10^{-3}$ | Hydrocyanic acid         | HCN               | $4.0 \times 10^{-10}$ |
| Hydrofluoric acid     | HF                | $7.4 \times 10^{-4}$ | Hexaaquairon(II) ion     | $Fe(H_2O)_6^{2+}$ | $3.2 \times 10^{-10}$ |
| Formic acid           | $HCO_2H$          | $1.8 \times 10^{-4}$ | Hydrogen carbonate ion   | $HCO_3^-$         | $4.8 \times 10^{-11}$ |
| Benzoic acid          | $C_6H_5CO_2H$     | $6.3 \times 10^{-5}$ | Hydrogen phosphate ion   | $HPO_4^{2-}$      | $3.6 \times 10^{-13}$ |
| Acetic acid           | $CH_3CO_2H$       | $1.8 \times 10^{-5}$ | Water                    | $H_2O$            | $1.0 \times 10^{-14}$ |
|                       |                   |                      | Hydrogen sulfide ion     | $HS^-$            | $1 \times 10^{-19}$   |

Larger the  $K_a$ , the stronger the acid.

## 16.3 Acid and Base Strength

### Relationship Between $K_a$ and $K_b$ – Conjugate Acid-Base Pair



$$K_a K_b = K_w \rightarrow \text{for a conjugate Acid-Base pair.}$$

\*: Con anion acting as a base?  
We will address this in more detail shortly.



## 16.4 Estimating the pH of Acid and Base Solutions

### Strong Acid and Strong Base Solutions

What is the pH of an aqueous solution of  $1.15 \times 10^{-2}$  M hydrobromic acid?

|     |                        |                  |   |                               |   |                       |
|-----|------------------------|------------------|---|-------------------------------|---|-----------------------|
| HBr | +                      | H <sub>2</sub> O | = | H <sub>3</sub> O <sup>+</sup> | + | Br <sup>-</sup>       |
| I   | $1.15 \times 10^{-2}$  |                  |   | 0                             |   | 0                     |
| C   | $-1.15 \times 10^{-2}$ |                  |   | $1.15 \times 10^{-2}$         |   | $1.15 \times 10^{-2}$ |
| E   | 0                      |                  |   | $1.15 \times 10^{-2}$         |   | $1.15 \times 10^{-2}$ |

HBr : Strong Acid.  
↳ 100%

I : Initial concentrations  
C : Change in concentrations  
E : Equilibrium concentrations

$$[\text{H}_3\text{O}^+] = 1.15 \times 10^{-2}$$

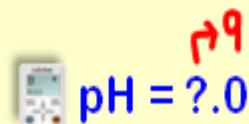
$$\begin{aligned}\text{pH} &= -\log_{10}(1.15 \times 10^{-2}) \\ &= 1.94\end{aligned}$$



## 16.4 Estimating the pH of Acid and Base Solutions

### Strong Acid and Strong Base Solutions

What is the pH of an aqueous solution of  $1.0 \times 10^{-5} \text{ M}$  sodium hydroxide?



| NaOH                    | + | = | Na <sup>+</sup>      | + | OH <sup>-</sup>      |
|-------------------------|---|---|----------------------|---|----------------------|
| I $1.0 \times 10^{-5}$  |   |   | O                    |   | O                    |
| C $-1.0 \times 10^{-5}$ |   |   | $1.0 \times 10^{-5}$ |   | $1.0 \times 10^{-5}$ |
| E O                     |   |   | $1.0 \times 10^{-5}$ |   | $1.0 \times 10^{-5}$ |

NaOH = Strong Base  
↳ Dissociates 100%

$$[\text{OH}^-] = 1.0 \times 10^{-5}$$

$$\text{pOH} = -\log_{10}(1.0 \times 10^{-5})$$

$$= 5$$

$$\begin{aligned}\text{pH} + \text{pOH} &= 14 \\ \text{pH} + 5 &= 14 \\ \text{pH} &= 9\end{aligned}$$

## 16.4 Estimating the pH of Acid and Base Solutions

### pH of a Weak Acid – Quadratic Equation

Calculate the pH of a 0.372 M aqueous solution of hypochlorous acid ( $\text{HClO}$ ,  $K_a = 3.5 \times 10^{-8}$ ).

| $\text{HClO}$ | +           | $\text{H}_2\text{O}$ | $\rightleftharpoons$ | $\text{H}_3\text{O}^+$ | + | $\text{ClO}^-$ |
|---------------|-------------|----------------------|----------------------|------------------------|---|----------------|
| I             | 0.372       |                      |                      | 0                      |   | 0              |
| C             | -x          |                      |                      | x                      |   | x              |
| E             | $0.372 - x$ |                      |                      | x                      |   | x              |

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]}$$

$$3.5 \times 10^{-8} = \frac{(x)(x)}{(0.372 - x)}$$

$$3.5 \times 10^{-8} = \frac{x^2}{(0.372 - x)}$$

$$3.5 \times 10^{-8}(0.372 - x) = x^2$$

$$x^2 + 3.58 \times 10^{-8}x - 1.302 \times 10^{-8} = 0$$

$$\left. \begin{array}{l} a = 1 \\ b = 3.58 \times 10^{-8} \\ c = -1.302 \times 10^{-8} \end{array} \right\} x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = 1.141 \times 10^{-4}, \quad -1.141 \times 10^{-4}$$

Disregard

$$x = 1.141 \times 10^{-4} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log_{10}(1.141 \times 10^{-4})$$

$$= 3.94$$

While this method is the most accurate but solving a quadratic can be problematic on 'bad math days' ... as in on exam days !!

## 16.4 Estimating the pH of Acid and Base Solutions

### pH of a Weak Acid – Approx Method

Calculate the pH of a 0.372 M aqueous solution of hypochlorous acid ( $\text{HClO}$ ,  $K_a = 3.5 \times 10^{-8}$ ).

| $\text{HClO}$ | +           | $\text{H}_2\text{O}$ | $\rightleftharpoons$ | $\text{H}_3\text{O}^+$ | + | $\text{ClO}^-$ |
|---------------|-------------|----------------------|----------------------|------------------------|---|----------------|
| I             | 0.372       |                      |                      | 0                      |   | 0              |
| C             | -x          |                      |                      | x                      |   | x              |
| E             | $0.372 - x$ |                      |                      | x                      |   | x              |

If  $[\text{HA}]_i > 100K_a$  then  $[\text{HA}]_i - x$  is  $\approx [\text{HA}]_i$

$$0.372 > 100(3.5 \times 10^{-8})$$

$$\text{thus } 0.372 - x \approx 0.372$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]}$$

$$3.5 \times 10^{-8} = \frac{x \cdot x}{0.372}$$

$$x^2 = 0.372(3.5 \times 10^{-8})$$

$$x = \sqrt{0.372(3.5 \times 10^{-8})}$$

$$x = 1.141 \times 10^{-4} = [\text{H}_3\text{O}^+]$$

$$\begin{aligned}\text{pH} &= -\log_{10}(1.141 \times 10^{-4}) \\ &= 3.94\end{aligned}$$

Short cut: So long as  $[\text{HA}]_i > 100K_a$

$$x = \sqrt{0.372(3.5 \times 10^{-8})}$$

$$x = \sqrt{[\text{HA}]_i K_a}$$