3/4/19

Autoionization of Water

- Water is amphoteric
- In pure water, a few molecules act as bases and a few act as acids
- This is referred to autoionization

$$H_2O\,(l) + H_2O\,(l) \rightleftharpoons OH^-\,(aq) + H_3O^+\,(aq)$$

equilibrium expression of autoionization of water:

$$K = [H_3O^+][OH^-] = K_w$$

ion product constant for water

@ 25°C, $K_w = 1.0 \times 10^{-14}$

Ion Product Constant

$K_w = [H_3O]^+[OH^-] = 1.0 \times 10^{-14}$ @ 25°C

$[H_3O^+] = [OH^-] \Rightarrow$ neutral

$[H^+] > [OH^-] \Rightarrow$ acidic

$[H^+] < [OH^-] \Rightarrow$ basic

ie. $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

$[H^+] = 1 \times 10^{-2}$

$[OH^-] = ?$ @ 25°C

$[OH^-] \cdot 1 \times 10^{-2} = 1 \times 10^{-14}$

$[OH^-] = 1 \times 10^{-12}$

pH Scale

- In pure water @ 25°C

$$[H_3O^+] = [OH^-] = 1 \times 10^{-7}\,M$$

- pH scale is a convenient way to report $[H_3O^+]$ in sln.

$$pH = -\log[H^+] \quad @\ 25°C$$

- neutral, pH = 7
- acidic, pH < 7
- basic, pH > 7

ie. $[H^+] = 1 \times 10^{-9}\,M$

$\Downarrow$

pH = 9

pOH scale (@ 25°C)

- Neutral, pOH = 7
- Acidic, pOH > 7
- Basic, pOH < 7

$$pH + pOH = 14$$

Relationship pH and pOH

$[H_3O^+][OH^-] = K_w = 1 \times 10^{-14}$

- Take $-\log$ of everything

$-\log[H_3O^+] + -\log[OH^-] = -\log K_w = 14.00$

- Result @ 25°C

$pH + pOH = pK_w = 14$

In class question: $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ + heat (endothermic)

increase temperature, shift right, so K_w INCREASE

K_w depends on temperature

In class question: pH goes down as temperature increases

Measuring pH

- pH meters
- Indicators: molecules that are one color in acidic form and another color in basic form

Strong Acids (SA)

- 7 strong acids: HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_3$, $HClO_4$
- Strong acids virtually completely dissociate in (aq) solution

ie. $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

- for monoprotic strong acids, assume

$[H_3O^+] = [acid]_0$

Calculating pH for SA

In class question: 1 drop of 2M HCl is added to 100 mL of water. pH?

→ $0.05 \times 10^{-3} L \times 2M = 1 \times 10^{-4}$ mol HCl = mol H_3O^+

one drop = 0.05 mL

$$\frac{1 \times 10^{-4} \text{ mol } H_3O^+}{0.1 \text{ L solution}} = 1 \times 10^{-3} M$$

$pH = 3$

$H_2O\ (l) + H_2O\ (l) \rightleftharpoons OH^-\ (aq) + H^+\ (aq)$

$\downarrow$

1×10^{-7} M @ 25°C

$\downarrow$

Ignore autoionization of water most of the time for SA problems

⊕ $HCl \to H^+ + Cl^-$ → shift left

Add HCl to beaker of water so that $[HCl] = 1 \times 10^{-9}$ M, pH?

$\left.\begin{array}{l} 1 \times 10^{-9}\text{M } H^+ \text{ from } HCl \\ 1 \times 10^{-7}\text{M } H^+ \text{ from water} \end{array}\right\}$ about 1×10^{-7} mol H^+ ⇒ pH ≈ 7

<u>Strong Bases</u> (SB)

- Strong bases are the soluble hydroxides, which are the alkali metal hydroxides (i.e. NaOH) and the heavier alkaline earth metal hydroxides (i.e. $Ca(OH)_2$)
- these substances completely dissociate in water (aq)

$NaOH(aq) \to Na^+(aq) + OH^-(aq)$

$Ca(OH)_2\ (aq) \to Ca^{2+}\ (aq) + 2OH^-\ (aq)$

ex) add 4.0g of NaOH to water so final volume is 1.0 L, pH?

$NaOH\ (aq) \to Na^+ (aq) + OH^- (aq)$

$[NaOH]_0 = [OH^-]\ (aq)$

$4.0\ g\ NaOH \times \frac{1\ mol}{40\ g} = 0.1$ mol in 1 L of sln.

$\frac{0.1\ mol\ NaOH}{L} = [OH^-] = 1 \times 10^{-1}\ M \to pOH = 1$

$pH = 13$

<u>Comparing SA and Weak Acids</u> (WA)

- SA completely dissociate to ions
- WA only partially dissociate to ions

<u>Comparing SB and Weak Bases</u> (WB

- SB completely dissociate to ions
- WB only partially dissociate to ions

$K_a = [H_3O^+][A^-]/[HA]$

How strong is a WA?

~~HA (aq)~~ For a WA, equation for dissociation is

$HA(aq) + H_2O\ (l) \rightleftharpoons H_3O^+ (aq) + A^-\ (aq)$

- The equilibrium constant for this rxn is K_a, acid dissociation constant