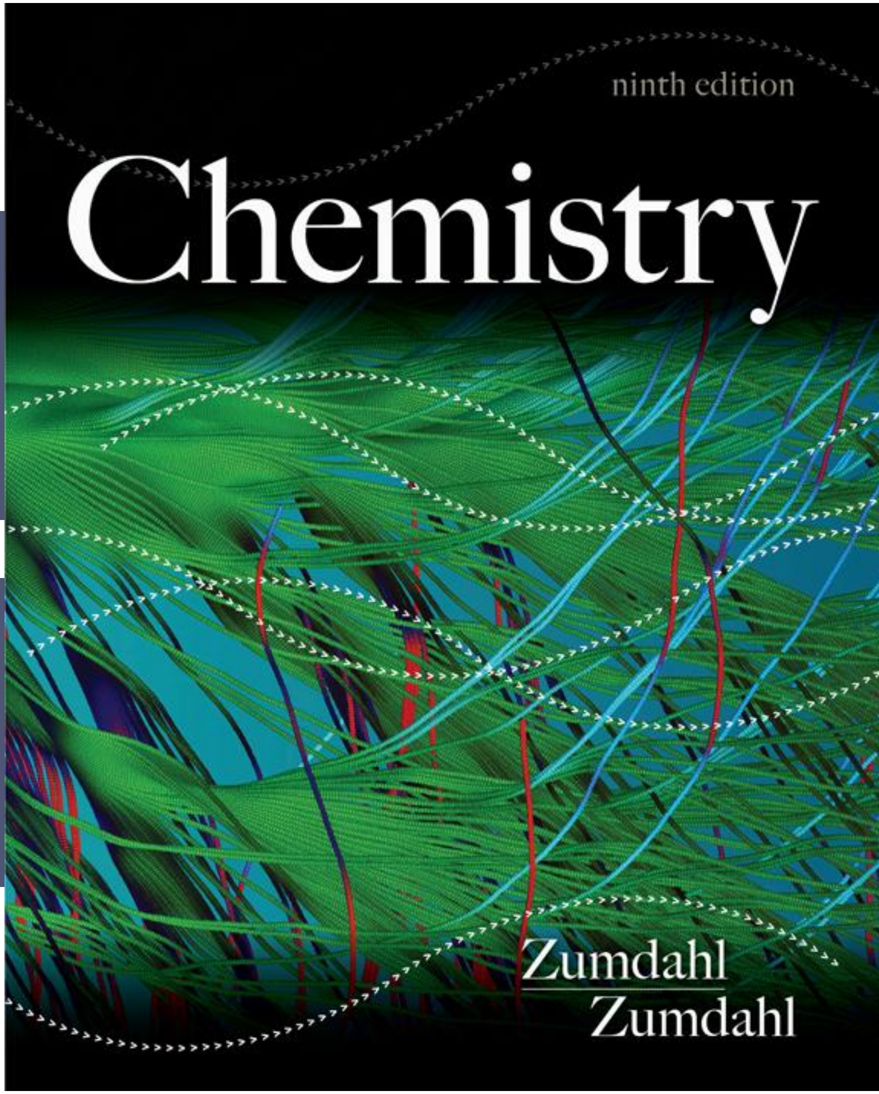


Chapter 14

Acids and Bases

Definitions of Acids and Bases

- Arrhenius:

  Acids produce H^+ ions in solution;

  Bases produce OH^- ions.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

$$NaOH_{(aq)} \rightarrow OH^-_{(aq)} + Na^+_{(aq)}$$

- Brønsted–Lowry:

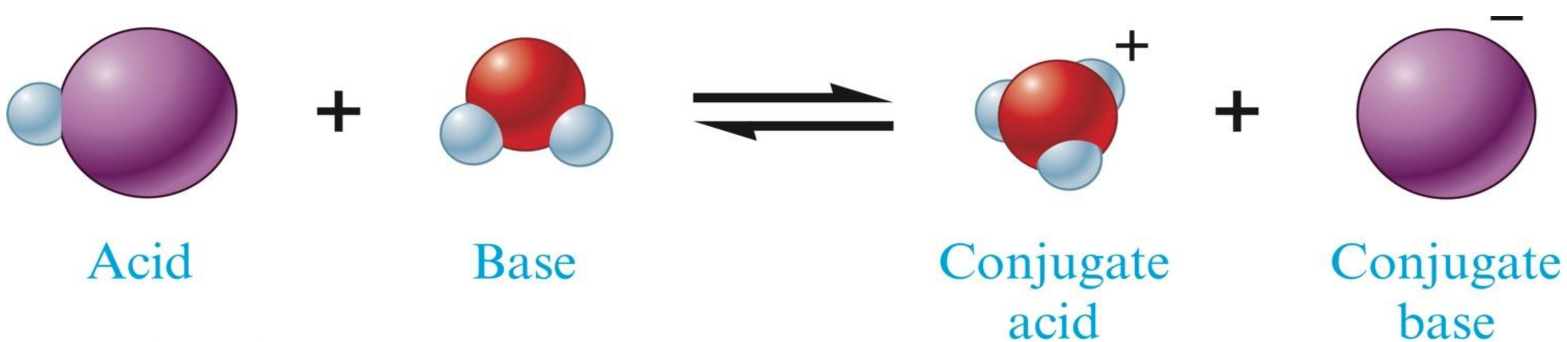
  Acids are proton (H^+) donors, bases are proton acceptors.

$$HCl + H_2O \rightarrow Cl^- + H_3O^+$$

acid base

Acid-base conjugate pair

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



- HA and A^- are acid/base conjugate pair.

  HA is the conjugate <u>acid</u> of the base A^-;
  A^- is the conjugate <u>base</u> of the acid HA
- Conjugate acid/base pair are related by **<u>one</u>** proton transfer.

- Strong acid:
  - Ionization equilibrium lies far to the right.
  - Yields a weak conjugate base.

$$HCl_{(aq)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$$

- Strong base: Yields a weak conjugate acid.

$$NaOH_{(aq)} \rightarrow OH^{-}_{(aq)} + Na^{+}_{(aq)}$$

- Weak acid:
  - Ionization equilibrium lies far to the left.
  - The weaker the acid, the stronger its conjugate base.

$$CH_3COOH_{(aq)} \rightleftharpoons H^{+}_{(aq)} + CH_3COO^{-}_{(aq)}$$

- Weak base: $NH_{3(aq)} + H_2O \rightleftharpoons NH_4^{+}{}_{(aq)} + OH^{-}_{(aq)}$

Examples of conjugate pairs:

- CH_3COOH/ CH_3COO^-
- NH_3/NH_4^+
- H_2SO_4/HSO_4^-
- $HSO_4^-/SO_4^=$

Water as an acid and a base

- Water is amphoteric: (Auto ionization)
  - Behaves either as an acid or as a base.
  - $H_2O_{(aq)} + H_2O_{(aq)} \rightleftharpoons H_3{}^{+}O_{(aq)} + OH^{-}_{(aq)}$
- At 25° C:

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

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

- In aqueous solutions the product of $[H^+]$ and $[OH^-]$ always equals to 1.0×10^{-14} at 25° C.

$$HA_{(aq)} + H_2O(l) \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

acid — base — conjugate acid — conjugate base

What is the equilibrium constant expression for an acid acting in water?

$$\boxed{K = \frac{[H_3O^+][A^-]}{[HA]}}$$

If the equilibrium lies to the right, the value for K_a is large (or >1)

If the equilibrium lies to the left, the value for K_a is small (or <1)

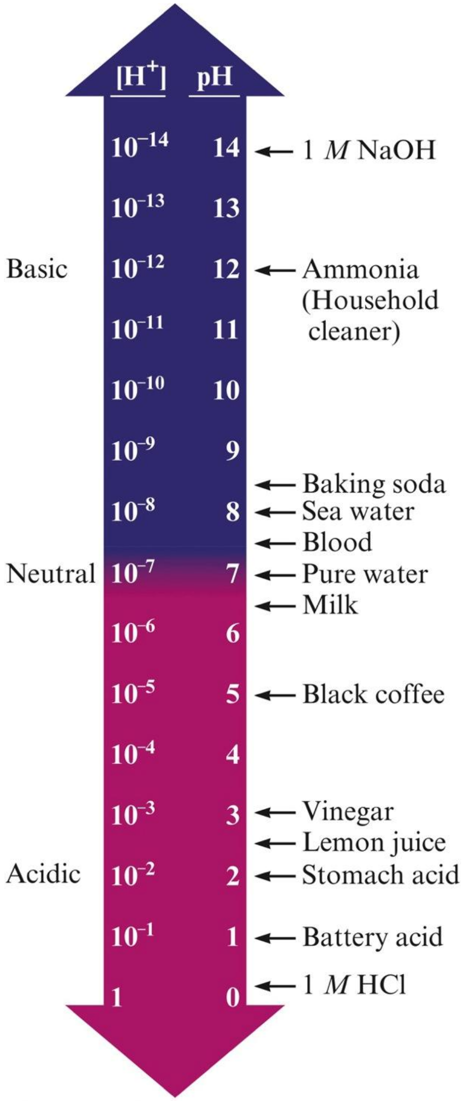
K_b *For bases*

Section 14.3
The pH Scale

- $pH = -\log[H^+]$, 0.1 M (pH=1) 0.01 M (pH=2)
- pH changes by 1 for every power of 10 change in $[H^+]$.
- A compact way to represent solution acidity.
- pH decreases as $[H^+]$ increases.
- Significant figures:
  - The number of decimal places in the log is equal to the number of significant figures in the original number.
  - $pNa^+ = -\log[Na^+]$

- pH = 7; neutral solution $-\log 1\times10^{-7} = 7$
- pH > 7; basic solution
  - The Higher the pH, The more basic the solution.
- pH < 7; acidic solution
  - Lower the pH, more acidic solution.

The pH Scale and pH Values of Some Common Substances



EXERCISE!

Calculate the pH for a solution of 1.0×10^{-4} M H^+?
(Use the calculator)

$$pH = -\log(1.0 \times 10^{-4}) = 4.00$$

Calculate: $[H^+]$, $[OH^-]$, pH, pOH

EXERCISE!

The pH of a solution is 5.85. What is the $[H^+]$ for this solution?

$pH = -\log [H^+] = 5.85$

$\log [H^+] = -5.85$

$[H^+] = \text{inv. log } (-5.85)$ *<u>(use the calculator)</u>*

$= 1.41 \times 10^{-6}\ M$

pH and pOH H^+ OH^-

- Recall:

$$K_w = [H^+][OH^-]$$

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

$$pK_w = pH + pOH$$

$$14.00 = pH + pOH$$

Calculate the pOH for each of the following solutions.

a) $1.0 \times 10^{-4}\ M\ H^+$

pH = - log (1.0×10^{-4}) = 4.00

pOH = 14.0 – pH = 14.0 – 4.0 = 10.00

b) $0.040\ M\ OH^-$

pOH = - log $[OH^-]$ = - log (0.040) = 1.40

The pH of a solution is 5.85. What is the $[OH^-]$ for this solution?

$[H^+]$= inv. log (-5.85) = …. = 1.41×10^{-6}

$[OH^-] = K_w/[H^+]$; *always* : $K_w = [H^+][OH^-]$

$= 1.00\times10^{-14}/1.41 \times 10^{-6}$

$= 7.09 \times 10^{-9}$ *M*

Consider an aqueous solution of 2.00×10^{-3} *M* HCl.

$$HCl_{(aq)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$$

Since HCl is strong acid, the major species in solution are:

$$H^{+}, Cl^{-}, H_2O$$

What is the pH?

$$pH = -\log[H^{+}] = -\log(2.00 \times 10^{-3})$$

$$= 2.70$$

Calculate the pH of a 1.5×10^{-2} *M* solution of HNO_3?

$[H^+]_{total} = [H^+]_{HNO_3} + [H^+]_{H_2O} \approx [H^+]_{HNO_3} = 1.5 \times 10^{-2}$

The major source for H^+ is from the nitric acid, HNO_3.

So:

$$pH = -\log(1.5 \times 10^{-2}) = 1.82$$

- *Important Note:* H_2SO_4

In aqueous solutions, the reaction of water dissociation below is always taking place.

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

But it is not always the main contributor of H^+ or OH^-.

Consider a 0.80 *M* aqueous solution of the weak acid HCN ($K_a = 6.2 \times 10^{-10}$).

$K_a >> K_w$, so, the second equilibrium below controls the pH.

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$ $K_w = 1.0 \times 10^{-14}$

$HCN_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CN^-_{(aq)}$ $K_a = 6.20 \times 10^{-10}$

0.800	0	0	*(initially)*
$(0.80 - x)$	x	x	*(at equilibrium)*

$K_a = x^2 / (0.80 - x)$; $x << 0.80$, so $0.80 - x \approx 0.80$

$6.20 \times 10^{-10} = x^2 / 0.800$

$x^2 = 4.69 \times 10^{-10}$

$x = 2.17 \times 10^{-5} = [H^+]$, pH = 4.66

Calculate the pH of a 0.50 *M* aqueous solution of the weak acid HF? ($K_a = 7.2 \times 10^{-4}$) **(YOU DO IT)**

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$ $K_w = 1.0 \times 10^{-14}$

$HF_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + F^-_{(aq)}$ $K_a = 7.2 \times 10^{-4}$

0.50	0	0	*(initially)*
(0.50 – x)	x	x	*(at equilibrium)*

The second reaction controls the pH.

0.50 is much smaller that x because K_a is very small.

$7.2 \times 10^{-4} = x^2 / 0.50$ $x = [H^+]$

$x^2 = 3.6 \text{ x } 10^{-4}$; $x = 0.019$; $pH = -\log(1.9 \text{ x } 10^{-2}) = 1.72$

Exercise:

A solution of 8.00 *M* formic acid (HCOOH) has $K_a = 1.8 \times 10^{-4}$, calculate its pH? **(YOU DO IT)**

$$HCOOH_{(aq)} \rightleftharpoons HCOO^-_{(aq)} + H^+_{(aq)}$$

$HCOO^-Na^+$

$$K_a = 1.8x10^{-4} = \frac{x^2}{8.00-x} \quad ; \quad x = [H^+] = 3.79x10^{-2}$$

Answer: pH=1.42

- Arrhenius: bases produce OH^- ions.
- Brønsted–Lowry: bases are proton acceptors.
- In a basic solution at 25° C, pH > 7.
- Ionic compounds containing OH^- are strong bases.
  - $LiOH$, $NaOH$, KOH, $Ca(OH)_2$
- $pOH = -\log[OH^-]$
- $pH = 14.00 - pOH$

Calculate the pH of a 2.0×10^{-3} *M* solution of sodium hydroxide.

$NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$ *(strong base)*

Since NaOH is strong, $[OH^{-}] = [NaOH] = 2.0 \times 10^{-3}$

$$[H^{+}] = \frac{K_w}{[OH^{-}]} = \frac{1.0x10^{-14}}{2.0x10^{-3}} = 5.0x10^{-12}$$

pH $= -\log[H^{+}] = -\log(5.0x10^{-12})$

$= 11.30$ *(basic)*

- pH calculations for solutions of <u>weak</u> bases are very similar to those for <u>weak</u> acids.
- $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$
- $pOH = -\log[OH^-]$
- $pH = 14.00 - pOH$

Equilibrium expression for weak bases uses K_b.

Calculate the pH of a 2.0 *M* solution of ammonia (NH_3).

$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$; $K_w = 1.0 \times 10^{-14}$

$NH_{3(aq)} + H_2O_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$; $K_b = 1.8 \times 10^{-5}$

2.0	0	0	*(initially)*
2.0 – x	x	x	*(at equilibrium)*

Approximations:

Reaction 2 controls the pH, and

x is much smaller than the initial concentration, 2.0 M

$$K_b = \frac{x^2}{2.0} = 1.8x10^{-5} \quad ; \quad x^2 = 3.6x10^{-5}$$

$$x = 6.0x10^{-3} = [OH^-] \quad ;$$

$$pOH = -\log(6.0x10^{-3}) = 2.22 \ ;$$

$$pH = 14.00 - 2.22 = 11.78$$ basic

Chemistry 113

General and Organic Chemistry for Students of Medicine

End of Chapter 14