Class 6.2

Acids and Bases

CHEM 102H

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Basic Definitions & Concepts

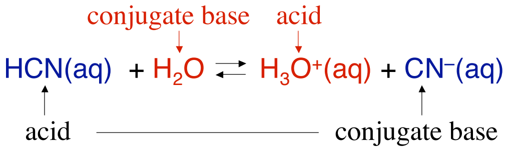
- Most basic concepts are given clearly in your text - these notes will only list these as topics discussed, so there will be less detail.
- Brønsted acids, bases (and distinction with Arrhenius and Lewis definitions)
- Strong acids and bases

  (eg., HCl, H_2SO_4; NaOH, KNH_2)

Basic Definitions & Concepts

- Weak acids and bases

  (eg., HCN, HF, CH_3COOH; NH_3, pyridine, CH_3NH_2)
- Conjugate acids and Bases, eg.,



$$\underset{\text{acid}}{HCN(aq)} + \overset{\text{conjugate base}}{H_2O} \rightleftarrows \overset{\text{acid}}{H_3O^+(aq)} + \underset{\text{conjugate base}}{CN^-(aq)}$$

Acidic and Basic Oxides

- The oxides that one uses to form acids and bases in aqueous solution often have reactivity that reflects their acidic or basic character.
- Examples: Li_2O, CaO, and BaO react with water to form basic solutions and can react with acids directly to form salts. Likewise, SO_3, CO_2, and N_2O_5 form acidic aqueous solutions and can react directly with bases to give salts.

Water Autoionization (Autoprotolysis)

Water self-dissociates, even in the absence of added acids or bases:

$$H_2O + H_2O \rightleftarrows H_3O^+(aq) + OH^-(aq)$$

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

- "$[H_2O]$" is constant, so $a_{H_2O} = 1$.
- In pure water, what are $[H_3O^+]$ & $[OH^-]$?
- What is ΔG° for this reaction?

pH *Scale*

H_3O^+ concentration is conveniently measured using the logarithmic pH scale:

$$\mathbf{pH} = -\log[H_3O^+]$$

- In pure H_2O,
  $[H_3O^+] = 10^{-7}$, $\mathrm{pH} = -\log 10^{-7} = 7$
- pOH is defined similarly: **pOH** = $-\log[OH^-]$

pH and pOH

pH = -log $[H_3O^+]$

pOH = -log $[OH^-]$

- In aqueous solutions, $[H_3O^+][OH^-] = 10^{-14}$
- This is true even with added acids or bases.

$$-\log \{[H_3O^+][OH^-]\} = -\log \{10^{-14}\}$$

$$-\log [H_3O^+] - \log [OH^-] = 14$$

pH + pOH = 14

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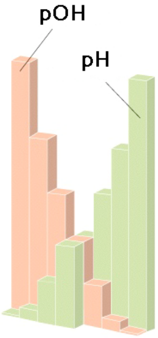
pH vs pOH



$$-\log \{[H_3O^+][OH^-]\} =$$

$$-\log \{10^{-14}\}$$

$$-\log [H_3O^+] - \log [OH^-] = 14$$

pH + pOH = 14

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pH for Strong Acids and Bases

There are only three cases where calculations differ:

(a) High concentrations - activities differ from concs. - we won’t worry about treating this case quantitatively

(b) Low to moderate concs. - very easy to handle (eg., pH of a 0.05 M strong acid or base)

(c) Very dilute conc. - e.g., 5 × 10^{-8} M LiOH

Acids - Definition of K_a

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

$$K_{eq} = \frac{[H_3O^+][A^-]}{[HA]} = K_a$$

- Once again, the water term is omitted in tabulating the equilibrium constants of acids.
- An <u>acid</u>, say HA, produces H_3O^+ in water. K_{eq} for an acid is called K_a.

Definition of K_b

Example:

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

- Again, "$[H_2O]$" is not included.

pH for Weak Acids and Bases

Success in calculations depends on skill in using approximations! What to remember:

(a) Except for <u>very dilute</u> solutions, $[OH^-]$ can be "initially neglected" in acidic solutions; $[H_3O^+]$ can be "initially neglected" in basic solutions

(b) At moderate to high concentrations, the percent dissociation is low

pH for Weak Acids and Bases

Even when approximations fail, remember what you have to use:

(a) Autoionization: K_w

(b) Equilibrium constants: K_a or K_b

(b) charge balance

(d) mass balance

Example 1

$CH_3COOH(aq) + H_2O \rightleftarrows H_3O^+(aq) + CH_3COO^-(aq)$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

- For acetic acid, pK_a = 4.74. What is the pH of a 0.1 M solution?

Example 2

$NH_3(aq) + H_2O \rightleftarrows NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

- For ammonia, pK_b = 4.74. What is the pH of a 0.1 M solution? What % of NH_3 is converted to NH_4^+?

Example 3

$HF(aq) + H_2O \rightleftarrows H_3O^+(aq) + F^-(aq)$

- For hydrofluoric acid, pK_a = 3.46. What is the pH of a 10^{-3} M solution?

Example 3 - Solution

$HF(aq) + H_2O \rightleftarrows H_3O^+(aq) + F^-(aq)$

$10^{-3} - x \qquad x \qquad x$

(Concentrations at equilibrium)

pK_a = 3.46;

$K_a = 3.47 \times 10^{-4}$

$$\frac{x^2}{10^{-3}-x} = 3.47\times10^{-4}$$

which expands to give

$$x^2 + (3.47\times10^{-4})x - 3.47\times10^{-7} = 0$$

$x = 4.4\times10^{-4}$ by quadratic formula

pH - case of high dilution

5×10^{-8} M LiOH - two sources of OH^-

$LiOH$ †→ $Li^+(aq) + OH^-(aq)$

$2\ H_2O \rightleftarrows H_3O^+(aq) + OH^-(aq)$

The set-up (what we know):

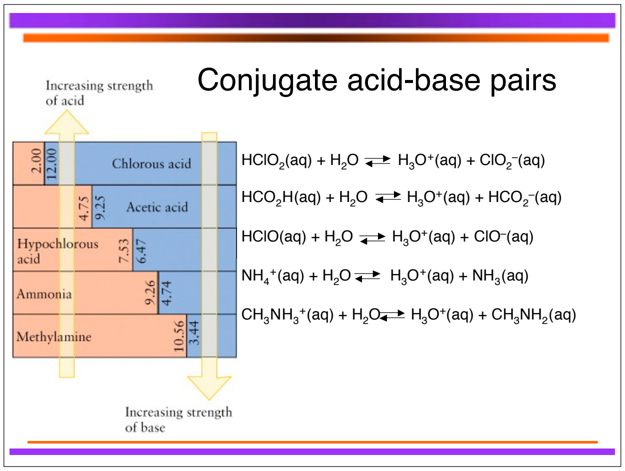
$[Li^+] = 5 \times 10^{-8}$; $[H_3O^+][OH^-] = 1 \times 10^{-14}$

Charge balance: $[OH^-] = [Li^+] + [H_3O^+]$

Solve, $[OH^-] = 1.2808 \times 10^{-7}$ pOH = 6.89

So, $[H_3O^+] = [OH^-] - [Li^+] = 0.7808 \times 10^{-7}$

pH = 7.11 (check: pH + pOH = 14)



Conjugate acid-base pairs

$HClO_2(aq) + H_2O \rightleftharpoons H_3O^+(aq) + ClO_2^-(aq)$

$HCO_2H(aq) + H_2O \rightleftharpoons H_3O^+(aq) + HCO_2^-(aq)$

$HClO(aq) + H_2O \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$

$NH_4^+(aq) + H_2O \rightleftharpoons H_3O^+(aq) + NH_3(aq)$

$CH_3NH_3^+(aq) + H_2O \rightleftharpoons H_3O^+(aq) + CH_3NH_2(aq)$