Chem 201 Lecture 10:

Equilibria. Week Acids

Textbook: Ch. 18 Ch. 17.5

WWW: search for “weak acid base ppt site:.edu”

Wiki: search for “weak acid”, “pH”

Presentations used to prepare this lecture:

1) *by Scott A. Sinex (Prince George's Community College)*

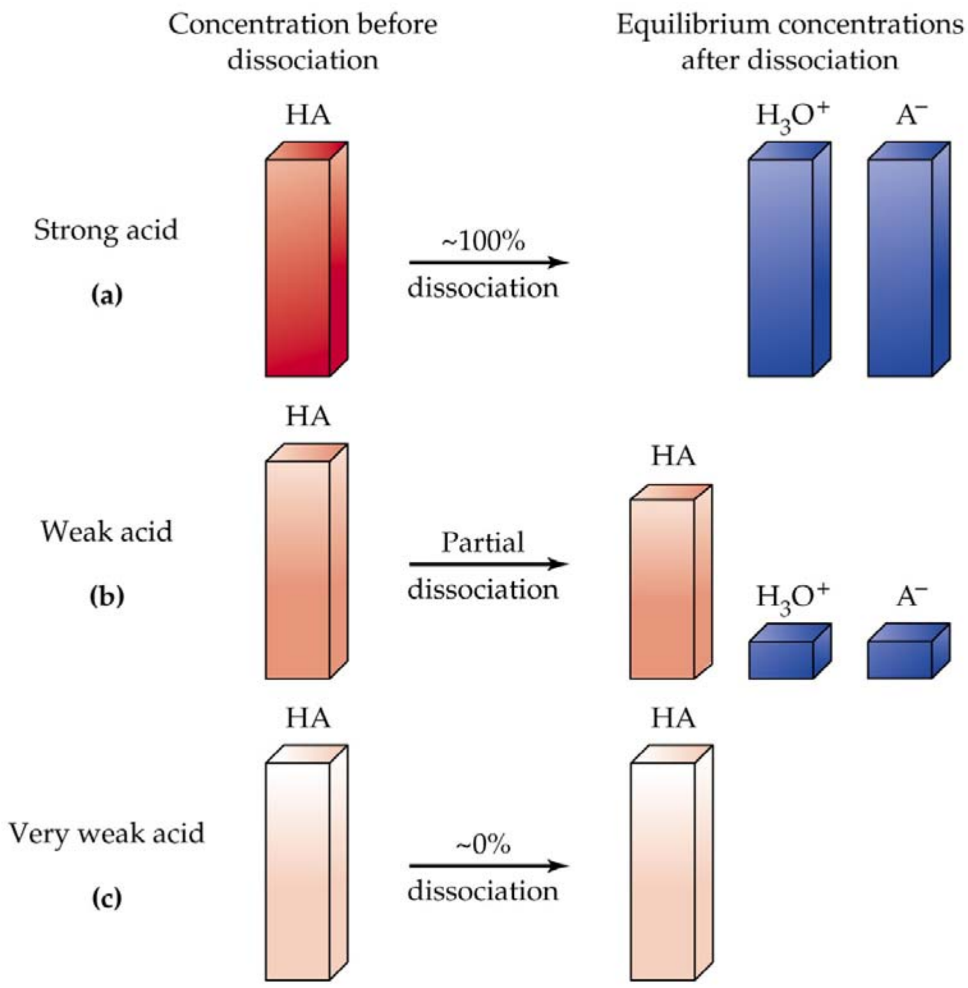
2) *by John D. Bookstaver & S.A. Green (St. Charles Community College)*

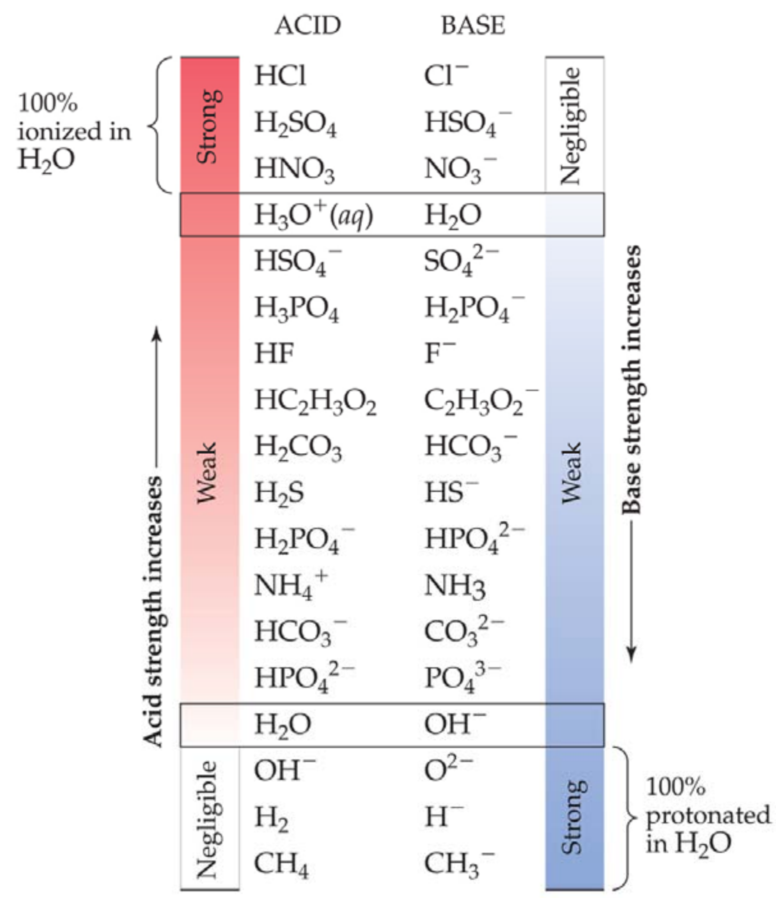
3) by Paul Charlesworth (Michigan Technological University)

Strength of Acids and Bases

- **Strong acids and bases:** are strong electrolytes that are assumed to ionize completely in water.
- **Weak acids and bases:** are weak electrolytes that ionize only to a limited extent in water.
- Solutions of weak acids and bases contain ionized and non-ionized species.

Acid Strength





Dissociation Constants

- For a generalized acid dissociation,

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

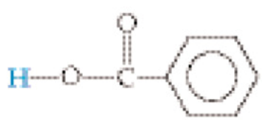
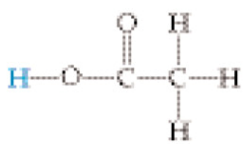
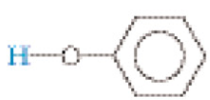
the equilibrium expression is

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

- This equilibrium constant is called the acid-dissociation constant, K_a.

Dissociation Constants

The greater the value of K_a, the stronger the acid.

Acid	Structural Formula	Conjugate Base	Equilibrium Reaction	K_a
Hydrofluoric (HF)		F^-	$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$	6.8×10^{-4}
Nitrous (HNO_2)		NO_2^-	$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$	4.5×10^{-4}
Benzoic ($HC_7H_5O_2$)		$C_7H_5O_2^-$	$HC_7H_5O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_7H_5O_2^-(aq)$	6.3×10^{-5}
Acetic ($HC_2H_3O_2$)		$C_2H_3O_2^-$	$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$	1.8×10^{-5}
Hypochlorous (HClO)		ClO^-	$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$	3.0×10^{-8}
Hydrocyanic (HCN)		CN^-	$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$	4.9×10^{-10}
Phenol (HC_6H_5O)		$C_6H_5O^-$	$HC_6H_5O(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq)$	1.3×10^{-10}

*The proton that ionizes is shown in blue.

Strength of Acids and Bases

- Stronger acid + stronger base $\rightarrow$

  weaker acid + weaker base

- Predict the direction of the following:

  $HNO_2(aq) + CN^-(aq) \rightleftharpoons HCN(aq) + NO_2^-(aq)$

  $HF(aq) + NH_3(aq) \rightleftharpoons F^-(aq) + NH_4^+(aq)$

pH – A Measure of Acidity

- The pH of a solution is *the negative logarithm of the hydrogen ion concentration (in mol/L)*.

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

$$pH + pOH = 14$$

Acidic solutions:	$[H^+] > 1.0 \times 10^{-7}$ M,	$pH < 7.00$
Basic solutions:	$[H^+] < 1.0 \times 10^{-7}$ M,	$pH > 7.00$
Neutral solutions:	$[H^+] = 1.0 \times 10^{-7}$ M,	$pH = 7.00$

Dissociation Constants. Acids

- For a generalized acid dissociation,

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the equilibrium expression is

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

- This equilibrium constant is called the acid-dissociation constant, K_a.

Dissociation Constants. Bases

$$\ddot{B} + H_2O \rightleftharpoons HB^+ + OH^-$$

The equilibrium constant expression for this reaction is

$$K_c = K_b = \frac{[HB^+][OH^-]}{[B]}$$

where K_b is the base-dissociation constant.

How do you solve the expression for either K or the equilibrium concentrations?

ICE Table

Initial concentration

change

Equilibrium concentration

Equilibrium concentration: general case

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

I	Initial	$[A]_0$	$[B]_0$	$[C]_0$	$[D]_0$
C	Change	$-ax$	$-bx$	$+cx$	$+dx$
E	Equilibrium	$[A]_0-ax$	$[B]_0-bx$	$[C]_0+cx$	$[D]_0+dx$

$$Keq = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{([C]_0+cx)^c\ ([D]_0+dx)^d}{([A]_0-ax)^a\ ([B]_0-bx)^b}$$

Solve for x or for Keq. Can be difficult!

Acid-base equilibria

- **Initial Change Equilibrium Table**: Determine the pH of 0.50 M HA solution at 25°C. K_a = 7.1 x 10^{-4}.

	$HA_{(aq)} \rightleftarrows$	$H^{+}_{(aq)}$ +	$A^{-}_{(aq)}$
Initial (M):	0.50	0.00	0.00
Change (M):	$-x$	$+x$	$+x$
Equilib (M):	$0.50-x$	x	x

$$\frac{x \times x}{0.5 - x} = \frac{x^2}{0.5 - x} = 7.1 \times 10^{-4}$$

How to solve?

1. Substitute new values into equilibrium expression.
2. If K_a is significantly (>1000 times) smaller than $[HA]_0$ the expression (0.50 – x) approximates to (0.50).
3. The equation can now be solved for x and pH.
4. If K_a is not significantly smaller than $[HA]_0$ the quadratic equation must be used to solve for x and pH.

Approximate solution:

$$\frac{x^2}{0.5 - x} \approx \frac{x^2}{0.5} = 7.1 \times 10^{-4} \qquad x \approx \sqrt{0.5 \times 7.1 \times 10^{-4}} = \boxed{0.0188}$$

pH of week acid solutions

- **The Quadratic Equation (accurate solution):**
- The expression must first be rearranged to:

$$ax^2 + bx + c = 0$$

- The values are substituted into the quadratic and solved for a positive solution to *x* and pH.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\frac{x^2}{0.5 - x} = 7.1\times10^{-4} \qquad x^2 + 7.1\times10^{-4}x - 3.55\times10^{-4} = 0$$

$$x = \frac{-7.1\times10^{-4} \pm \sqrt{(7.1\times10^{-4})^2 - 4\times3.55\times10^{-4}}}{2}$$

$$x = 0.0185$$

$$x = -0.0192$$

pH of week acid solutions

Accurate: **x= 0.0185**

Approximate: **x= 0.0188**

Approximate solution is quite good! (<2% error)

Excel sheet!

Acid Ionization Constants

- **Percent Dissociation:** A measure of the strength of an acid.

$$\%\ \text{Dissociation} = \frac{[\text{H}^+]}{[\text{HA}]_0} \times 100\%$$

- Stronger acids have higher percent dissociation.
- Percent dissociation of a weak acid decreases as its concentration increases.

Additional problems

- Calculate the pH of a 0.036 M nitrous acid (HNO_2) solution.
- What is the pH of a 0.122 M monoprotic acid whose K_a is 5.7×10^{-4}?
- The pH of a 0.060 M weak monoprotic acid is 3.44. Calculate the K_a of the acid.