# Acid/Base Strengths

**acid strength** – determined by extent of reaction of acid with water to form $H_3O^+(aq)$, or the extent of its ionization or dissociation, as shown by the magnitude of its equilibrium constant, $K_a$ – then for any hydrogen-containing compound, HA

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

**EQUATION FOR ACIDITY FOR ANY HA**

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

**EQUILIBRIUM CONSTANT**

**base strength** – (aside from Group I and II hydroxides) determined by extent of reaction of base with water to form $OH^-(aq)$, or extent of its ionization, as shown by the magnitude of its equilibrium constant, $K_b$ – then for any base B:

$$B{:}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + BH^+(aq)$$

**EQUATION FOR BASICITY FOR ANY B:**

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

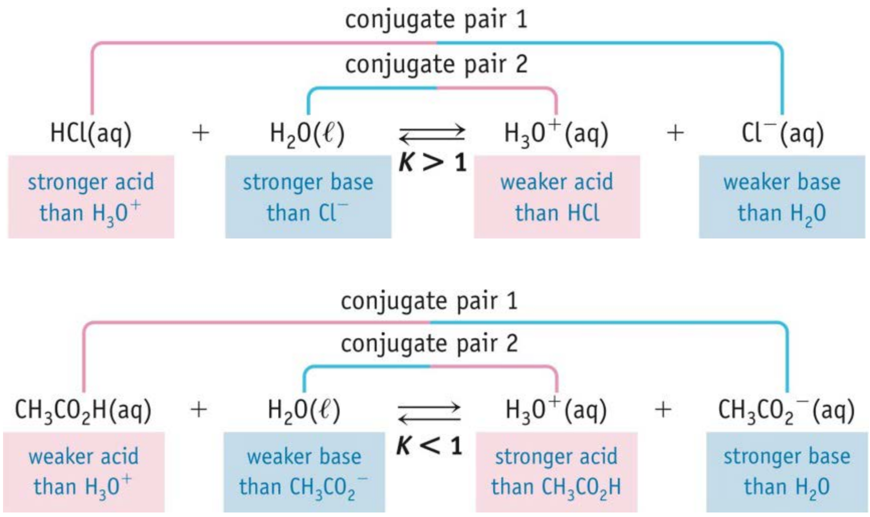
**EQUILIBRIUM CONSTANT**

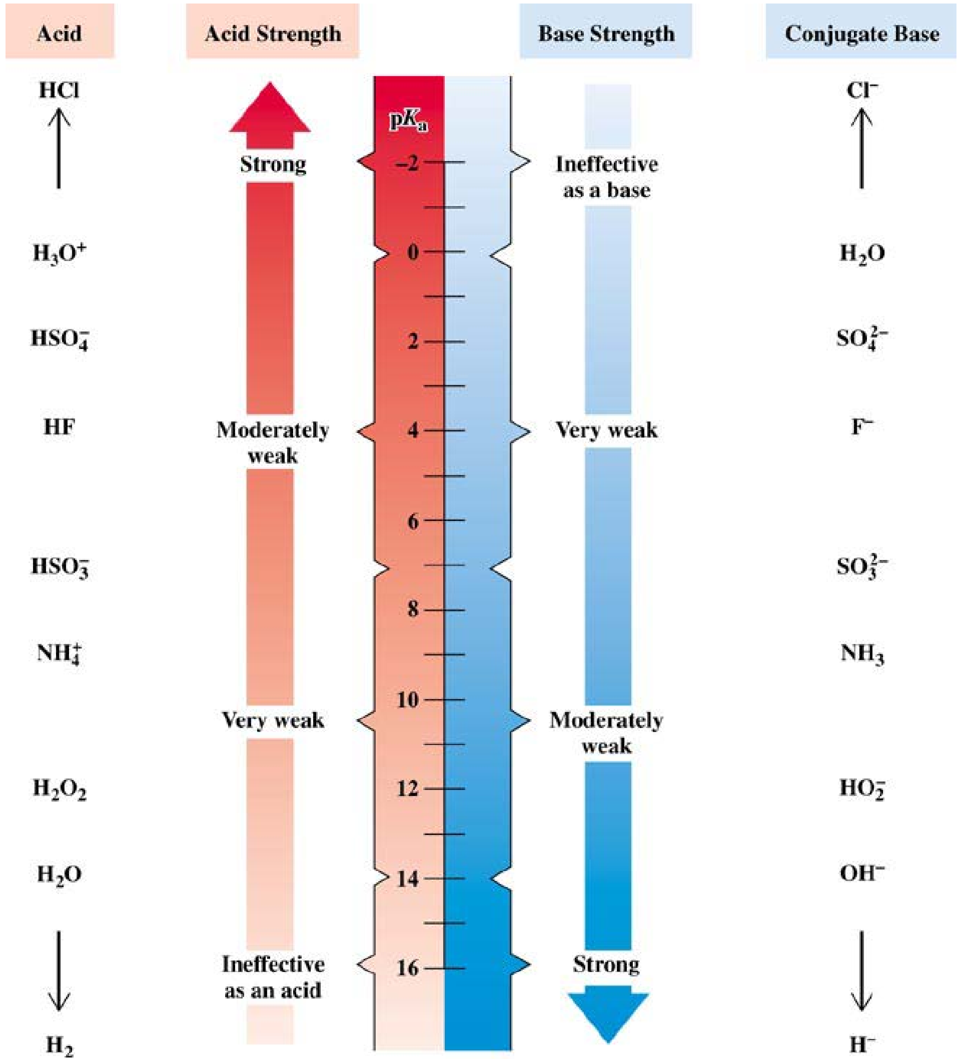
# Conjugate Acid/Base Pairs

The conjugate base of a weak acid is a weak base. The weaker the acid, the stronger the base. However, if one member of a conjugate pair is weak, so is its conjugate.

The relation between $K_a$ for an acid and $K_b$ for its conjugate base in aqueous solution is $K_w = K_a \times K_b$.

When a strong acid (or base) is added to a weak base (or acid), they react nearly completely.



# Water and the pH Scale

water autoionization: $2\ H_2O(l) \Leftarrow\Rightarrow H_3O^+(aq) + OH^-(aq)$

$$K_w = [H_3O^+][OH^-] = 1.01 \times 10^{-14} \text{ (at 25°C)}$$

$K_w$ equilibrium constant which depends upon temperature.

| Temperature Dependence of $K_w$ | |
|---|---|
| **Temperature (°C)** | **$K_w$** |
| **0** | $0.114 \times 10^{-14}$ |
| **10** | $0.292 \times 10^{-14}$ |
| **20** | $0.681 \times 10^{-14}$ |
| **25** | $1.01 \times 10^{-14}$ |
| **30** | $1.47 \times 10^{-14}$ |
| **40** | $2.92 \times 10^{-14}$ |
| **50** | $5.47 \times 10^{-14}$ |
| **60** | $9.61 \times 10^{-14}$ |

**pH is temperature dependent**

| condition | concentrations | pH (only at 25°C) |
|---|---|---|
| acidic | $[H_3O^+] > [OH^-]$ | pH < 7 |
| neutral | $[H_3O^+] = [OH^-]$ | pH = 7 |
| basic | $[H_3O^+] < [OH^-]$ | pH > 7 |

significant figures for logarithms:

3 significant digits | 3 decimal places

$$\log 1.00 \times 10^{-3} = 3.000$$

# Systematic Treatment of Equilibrium

GOAL - account for the concentration of all species present in a solution once equilibrium has been reached. The equations to do this derive from

1. charge balance - solution must be electrically neutral
2. material balance - conservation of matter; what happens to initial concentrations
3. equilibrium expressions and their equilibrium constants

# Systematic Treatment of Equilibrium – Charge Balance

**Charge balance** is an algebraic statement of electroneutrality.

sum of + charges = sum of – charges

**EX 1.** Write the charge balance for a solution containing only the following ions:

$H^+$, $OH^-$, $Na^+$, $Ba^{2+}$, $PO_4^{3-}$, $Ag^+$, $SO_4^{2-}$

$$[H^+] + [Na^+] + 2\,[Ba^{2+}] + [Ag^+] = [OH^-] + 3\,[PO_4^{3-}] + 2\,[SO_4^{2-}]$$

# Systematic Treatment of Equilibrium – Charge Balance

**salt**

**EX 2.** Write the charge balance for a solution containing $(NH_4)_3PO_4$. Be sure to consider all possible equilibrium reactions.

$NH_4^+$ is an acid but its equilibrium reaction produces its neutral conjugate base, $NH_3$; $PO_4^{3-}$ is a base whose equilibrium reactions produce

$$PO_4^{3-} + H_2O \Leftrightarrow OH^- + HPO_4^{2-}$$
$$HPO_4^{2-} + H_2O \Leftrightarrow OH^- + H_2PO_4^-$$
$$H_2PO_4^- + H_2O \Leftrightarrow OH^- + H_3PO_4$$

in aqueous solution autoionization of water must always be considered: $H_2O + H_2O \Leftrightarrow H_3O^+ + OH^-$

$$[NH_4^+] + [H^+] = [OH^-] + [H_2PO_4^-] + 2\,[HPO_4^{2-}] + 3\,[PO_4^{3-}]$$

# Molarity and Formality

These two types of concentration are identical for a species which does not dissociate into ions in solution or does not react with water to produce ions

**Molarity** is the concentration of the species that is actually present in solution such as 1.0 M $Cl^-$.

Consider a species which forms ions in solution such as acetic acid, $CH_3COOH$. You might try to place exactly 1.0 mole in a liter of water to form a 1.0 M solution but the solution will have partially dissociated into $CH_3COO^-$. Such a solution is 1.0 F = $[CH_3COOH] + [CH_3COO^-]$. So **formality** represents the concentration of the different "pieces" that acetic acid forms in solution or the concentration originally placed in water (before dissociation).

Harris uses formality

# Systematic Treatment of Equilibrium – Mass Balance

**EX 3.** What is the mass balance equation for a solution prepared by adding 0.100 moles of ammonia to 1.000 L?

$NH_3$ is a weak base and reacts with water:

$$NH_3(aq) + H_2O\,(l) \;\Leftrightarrow\; OH^-(aq) + NH_4^+(aq)$$

so the mass balance is

$$\mathbf{0.100\ F = [NH_3]_o = [NH_3] + [NH_4^+]}$$

# Systematic Treatment of Equilibrium

equations needed for solution for unknown

General approach includes

1. write down the pertinent chemical reactions and their equilibrium constant expressions
2. write down all species present in solution according to #1
3. set up the charge balance equation (the solution must be electrically neutral so the number of positive charges = the number of negative charges)
4. apply the material balance equation (conservation of matter) – may be more than one
5. are there enough equations to solve for the unknowns?

# Systematic Treatment – Dilute Strong Acid

**EX 4.** What is the pH of a $1.0 \times 10^{-8}$ M solution of HBr?

1. reactions, $K$ ($HBr \rightarrow H^+ + Br^-$)
   $H_2O \Leftrightarrow H^+ + OH^-$ $\quad K_w = [H^+][OH^-]$
2. species: $H^+$, $OH^-$, $Br^-$
3. charge balance: $[H^+] = [OH^-] + [Br^-]$
4. mass balance: $[Br^-] = 1.0 \times 10^{-8}$

substitute for $[OH^-]$ $\qquad$ substitute for $[Br^-]$

$$K_w = [H^+][OH^-] = [H^+]\{[H^+] - [Br^-]\} = [H^+]^2 - [H^+][Br^-]$$

quadratic: $[H^+]^2 - [H^+][Br^-] - K_w = 0$

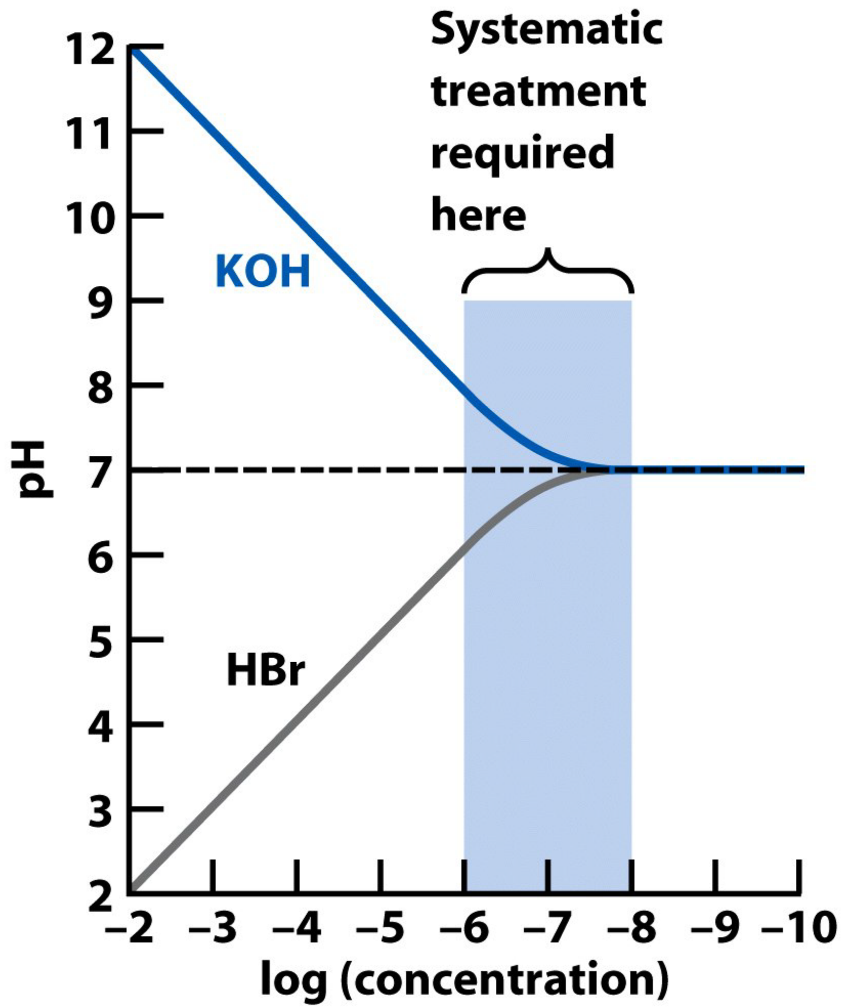
$$[H^+] = \{-10^{-8} \pm \sqrt{[(10^{-8})^2 + 4(1.01 \times 10^{-14})]}\} / 2$$

$$= 1.05 \times 10^{-8}\ \text{M}$$

$\Rightarrow$ pH = 6.978 $\Rightarrow$ **6.98**

# Systematic Treatment – Dilute Strong Acid/Base

For dilute strong acids or bases a systematic treatment is only required when the concentration is between ~ $10^{-8}$ and $10^{-6}$ M. Above $10^{-8}$ one cannot practically make such a dilute solution and below $10^{-6}$ $H^+$ from $K_w$ is too small a contribution.



# Systematic Treatment – Weak Acid/Base

**FOR LAB THIS WEEK**

The acidity of an aqueous solution of $CH_3COOH$ is determined by its reaction with water:

$$CH_3COOH(aq) + H_2O(l) <=> H_3O^+(aq) + CH_3COO^-(aq)$$

and quantitatively measured by its acid dissociation constant, $K_a$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

where all concentrations are obtained at equilibrium.

# Systematic Treatment – Weak Acid/Base

1. reactions

$H_2O$ <=> $H^+ + OH^-$ $K_w = [H^+][OH^-]$

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**$CH_3COOH$ is an acid so $[OH^-] \ll [H^+]$**

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$$= \frac{[H^+]\{[H^+] - K_w/[H^+]\}}{0.01 - \{[H^+] - K_w/[H^+]\}}$$

$$= \frac{[H^+]^2}{0.01 - [H^+]} \Rightarrow \boxed{K = \frac{x^2}{F - x}}$$

# Systematic Treatment – Weak Acid/Base

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$$= \frac{[H^+]\{[H^+] - [OH^-]\}}{0.01 - \{[H^+] - [OH^-]\}}$$

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$$= \frac{[H^+]^2}{0.01 - [H^+]} \Rightarrow K = \frac{x^2}{F - x}$$

**COMPARE WITH ICE TABLE**

# Weak Acid - $K_a = x^2 / (F - x)$

**EX 6.** What is the pH of 0.050 M solution of a weak acid, $K_a = 1.59 \times 10^{-10}$?

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|---|---|---|---|---|---|
| I | 0.050 M | | | ∼ 0 | 0 |
| C | $-x$ | | | $+x$ | $+x$ |
| E | $0.050 - x$ | | | $x$ | $x$ |

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$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x^2}{0.050 - x}$$

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|---|---|---|---|
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$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x^2}{0.050 - x}$$

quadratic: $x^2 + K_a x - 0.050 K_a = 0$

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$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x^2}{0.050 - x}$$

quadratic: $x^2 + K_a x - 0.050 K_a = 0$

$$x = \{-1.59 \times 10^{-10} \pm \sqrt{[(1.59 \times 10^{-10})^2 + 4(0.050)(1.59 \times 10^{-10})]}\} / 2$$

$= 2.819 \times 10^{-6}$ M

=> pH = 5.5498 => **5.55**

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|---|---|---|---|---|
| I | 0.050 M | | ~ 0 | 0 |
| C | $- x$ | | $+ x$ | $+x$ |
| E | $0.050 - x$ | | $x$ | $x$ |

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x^2}{0.050 - x}$$

quadratic: $x^2 + K_a x - 0.050 K_a = 0$

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$= 2.819 \times 10^{-6}$ M

=> pH = 5.5498 => **5.55**

**$(2.819 \times 10^{-6}) / 0.050$**
**< 1%**
**$x = \sqrt{(0.050\ K_a)}$**

**1% (5%) Rule**