# Acid-Base Chemistry

Varying Definitions, depends on context/application

| | Acid | Base |
|---|---|---|
| Arrhenius | | |
| | | |
| Brönsted/Lowry | | |
| | | |
| Lewis | | |
| | | |

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# Key Considerations

**Autoprotolysis of Water**

- Water is an <u>**amphiprotic**</u> substance: can behave as either an acid or base.

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

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$$

- Important to keep this in mind!

**Conjugate Acid/Base Pairs:**

- Species that differ by one $H^+$

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

- When an acid dissociates to lose a proton, it forms a conjugate base
- When a base accepts a proton, it forms a conjugate acid

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## Acid/Base Strength

"Strength" = measure of efficiency of production of $H^+$ (or $OH^-$), extent of dissociation.

$$HA + H_2O \rightleftarrows H_3O^+ + A^-$$

**Strong** Acids (or Bases) dissociate completely in water

- Very large K for dissociation

**Weak** Acids (or Bases) only dissociate partially

- Very small K for dissociation

What does this mean for the conjugate base (acid)?

- See **Table 16.1**

**TABLE 16.2 The Common Strong Acids and Strong Bases**

| Acids | Bases |
|---|---|
| $HCl$ | $LiOH$ |
| $HBr$ | $NaOH$ |
| $HI$ | $KOH$ |
| $HClO_4$ | $RbOH$ |
| $HNO_3$ | $CsOH$ |
| $H_2SO_4$[a] | $Mg(OH)_2$ |
| | $Ca(OH)_2$ |
| | $Sr(OH)_2$ |
| | $Ba(OH)_2$ |

[a] $H_2SO_4$ ionizes in two distinct steps. It is a strong acid only in its first ionization

- Know strong acids/bases assume everything else is weak! ($H_2SO_4$, $HCl$, $HNO_3$, $HClO_4$, $NaOH$, $KOH$, $LiOH$ **Table 16.2**)
- The strongest acid/base determines the tendency (direction) of the reaction



## Acid/Base Strength

**TABLE 16.1 Relative Strengths of Some Common Brønsted–Lowry Acids and Bases**

| Acid | | Conjugate Base | |
|---|---|---|---|
| Perchloric acid | $HClO_4$ | Perchlorate ion | $ClO_4^-$ |
| Hydroiodic acid | $HI$ | Iodide ion | $I^-$ |
| Hydrobromic acid | $HBr$ | Bromide ion | $Br^-$ |
| Hydrochloric acid | $HCl$ | Chloride ion | $Cl^-$ |
| Sulfuric acid | $H_2SO_4$ | Hydrogen sulfate ion | $HSO_4^-$ |
| Nitric acid | $HNO_3$ | Nitrate ion | $NO_3^-$ |
| Hydronium ion[a] | $H_3O^+$ | Water[a] | $H_2O$ |
| Hydrogen sulfate ion | $HSO_4^-$ | Sulfate ion | $SO_4^{2-}$ |
| Nitrous acid | $HNO_2$ | Nitrite ion | $NO_2^-$ |
| Acetic acid | $HC_2H_3O_2$ | Acetate ion | $C_2H_3O_2^-$ |
| Carbonic acid | $H_2CO_3$ | Hydrogen carbonate ion | $HCO_3^-$ |
| Ammonium ion | $NH_4^+$ | Ammonia | $NH_3$ |
| Hydrogen carbonate ion | $HCO_3^-$ | Carbonate ion | $CO_3^{2-}$ |
| Water | $H_2O$ | Hydroxide ion | $OH^-$ |
| Methanol | $CH_3OH$ | Methoxide ion | $CH_3O^-$ |
| Ammonia | $NH_3$ | Amide ion | $NH_2^-$ |

Increasing acid strength

Increasing base strength

[a] The hydronium ion–water combination refers to the ease with which a proton is passed from one water molecule to another; that is, $H_3O^+ + H_2O \rightleftharpoons H_2O + H_3O^+$

## Solution Acidity and pH

- Because water is amphiprotic, "pure" water will contain a small amount of OH- and H+

$$H_2O \rightleftarrows H^+ + OH^-$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ (at } 25^oC)$$

EXAMPLE: What is the $[H^+]$ in "pure" water?

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## Solution Acidity and pH

**pH is a measure of $[H^+]$ (actually activity)**

$$pH = -\log A_{H+} \approx -\log[H^+]$$

NOTE: you can "p" almost anything!

**Acidity and basicity use "pure" water as a reference**

| Solution | $[H^+]$ | $[OH^-]$ | pH |
|---|---|---|---|
| Neutral | $= 1.0 \times 10^{-7}$ M | $= 1.0 \times 10^{-7}$ M | |
| Acidic | $> 1.0 \times 10^{-7}$ M | $< 1.0 \times 10^{-7}$ M | |
| Basic | $< 1.0 \times 10^{-7}$ M | $> 1.0 \times 10^{-7}$ M | |

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# Useful Things to Remember

1. $K_a$ for an acid and $K_b$ for its conjugate base are related!

| | |
|---|---|
| $HA \rightleftarrows H^+ + A^-$ | |
| $A^- + H_2O \rightleftarrows HA + OH^-$ | |
| | |

*In general: $K_aK_b = K_w$ for conjugate acid/base pairs!*

2. pH and pOH are related!

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

3. As [H+] increases, [OH-] decreases (& vice versa)
   - Kw must be satisfied!!!

4. If you know pH, you also must know pOH, [H+], and [OH-]
   - $K_w$ rules!
   - $[H+] = 10^{-pH}$…



# $K_a$, $K_b$ and pH

**Example: What is the pH of a 0.10 M solution of acetic acid ($K_a$ = 1.8 x $10^{-5}$)?**

**Example: A 0.10 M solution of propanoic acid has a pH of 2.94. What is the value of $K_a$ for propanoic acid?**

$$CH_3CH_2COOH + H_2O \rightleftarrows CH_3CH_2COO^- + H_3O^+$$

**Rule of Thumb: If $100K_a < [HA]_{initial}$, assume $x << [HA]_{initial}$**
- avoids quadratic, saves a little math
- quadratic always works!

## $K_a$, $K_b$ and pH

Use the same approach for bases and acidic(basic) salts

$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$ $K_b = 1.8 \times 10^{-5}$

KCN: $CN^- + H_2O \rightleftarrows HCN + OH^-$ $K_b = 2.5 \times 10^{-5}$

– Remember conjugate acid/base concepts

**Example: What is the pH of a solution that is 0.10 M KCN?**

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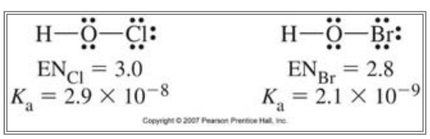
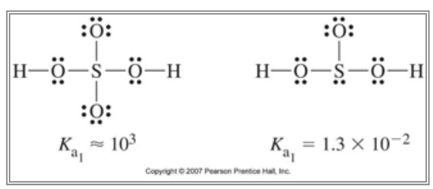
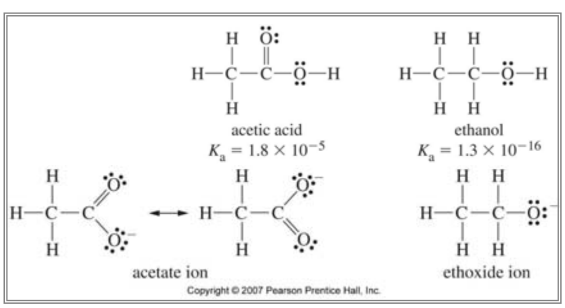
## Structure-Acidity Relationships

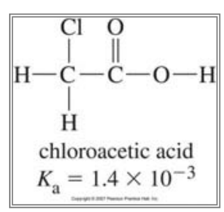
Strength of an acid depends on:

– How tightly the proton is held
– Stability of the conjugate base

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## Dealing with Mixtures and Polyprotics

- There can only be one $[H^+]$ in solution! (or [anything] for that matter) At equilibrium, all K's are satisfied.
- This can make things hairy! Look for simplification! Remember, you understand some chemistry!

**Example: Consider a solution that contains 0.10M each of HF ($K_a$ =7.2 x $10^{-4}$), HCN ($K_a$ = 6.2 x $10^{-10}$) and Phenol ($K_a$ = 1.6 x $10^{-10}$). What is the pH of this solution?**

$$HF \rightleftarrows H^+ + F^-$$
$$HCN \rightleftarrows H^+ + CN^-$$
$$C_6H_5OH \rightleftarrows H^+ + C_6H_5O^-$$

**Polyprotic acids and bases:**

- **REMEMBER**: Each successive step gets weaker!

**Example: Calculate the pH of a 0.10 M solution of Oxalic Acid ($H_2C_2O_4$, $pK_{a1}$ = 1.23, $pK_{a2}$ = 4.19).**

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## Systematic Approach to Simultaneous Equilibria

**Example revisited: A solution contains 0.10M each of HF ($K_a$=7.2 x $10^{-4}$), HCN ($K_a$=6.2 x $10^{-10}$) and Phenol ($K_a$=1.6 x $10^{-10}$). What is the pH of this solution?**

How might we treat this rigorously? Four equilibria to consider:

$$HF \rightleftarrows H^+ + F^- \qquad K_1 = 7.2 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]}$$
$$HCN \rightleftarrows H^+ + CN^- \qquad K_2 = 6.2 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]}$$
$$HA \rightleftarrows H^+ + A^- \qquad K_3 = 1.6 \times 10^{-10} = \frac{[H^+][A^-]}{[HA]}$$
$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$$

Eight unknowns, we need eight equations, where will we get 4 more? Remember, this is chemistry!

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## Systematic Approach to Simultaneous Equilibria

**Charge Balance:** solutions must be neutral [+] = [-]

– **Only one** charge balance equation exists for the system!

**Mass Balance:** # moles of each <u>atom</u> cannot change!

– **Multiple** mass balance equations **may** exist for the system.

Lots of algebra later gets us a tough equation to solve!

– But we have the tools to do it!

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## Method of Successive Approximations

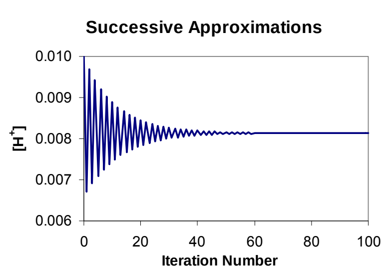
1. Make a guess,
2. Run calculation based on that guess,
3. Use result to make a new guess,
4. Repeat 2 and 3 until "convergence".

   Spreadsheets make this fairly easy.

$$[H^+] = \frac{0.10\,K_1}{[H^+]+K_1} + \frac{0.10\,K_2}{[H^+]+K_2} + \frac{0.10\,K_3}{[H^+]+K_3} + \frac{K_w}{[H^+]}$$

After about 100 iterations, we get convergence to [H+] = 0.008133 M, pH = 2.09

Ignoring everything but HF and solving quadratic gives [H+] = 0.008133 M, pH = 2.09



## One last thought

**What is the pH of $10^{-2}$M HCl?**

**What is the pH of $10^{-4}$M HCl?**

**What is the pH of $10^{-6}$M HCl?**

**What is the pH of $10^{-8}$M HCl?**

- **How do we treat this?**