Acids and Bases

Acid/Base Definitions

- Arrhenius Model
  - Acids produce hydrogen ions in aqueous solutions
  - Bases produce hydroxide ions in aqueous solutions
- Bronsted-Lowry Model
  - Acids are proton donors
  - Bases are proton acceptors
- Lewis Acid Model
  - Acids are electron pair acceptors
  - Bases are electron pair donors

Acid Dissociation

$HA \rightarrow H^+ + A^-$

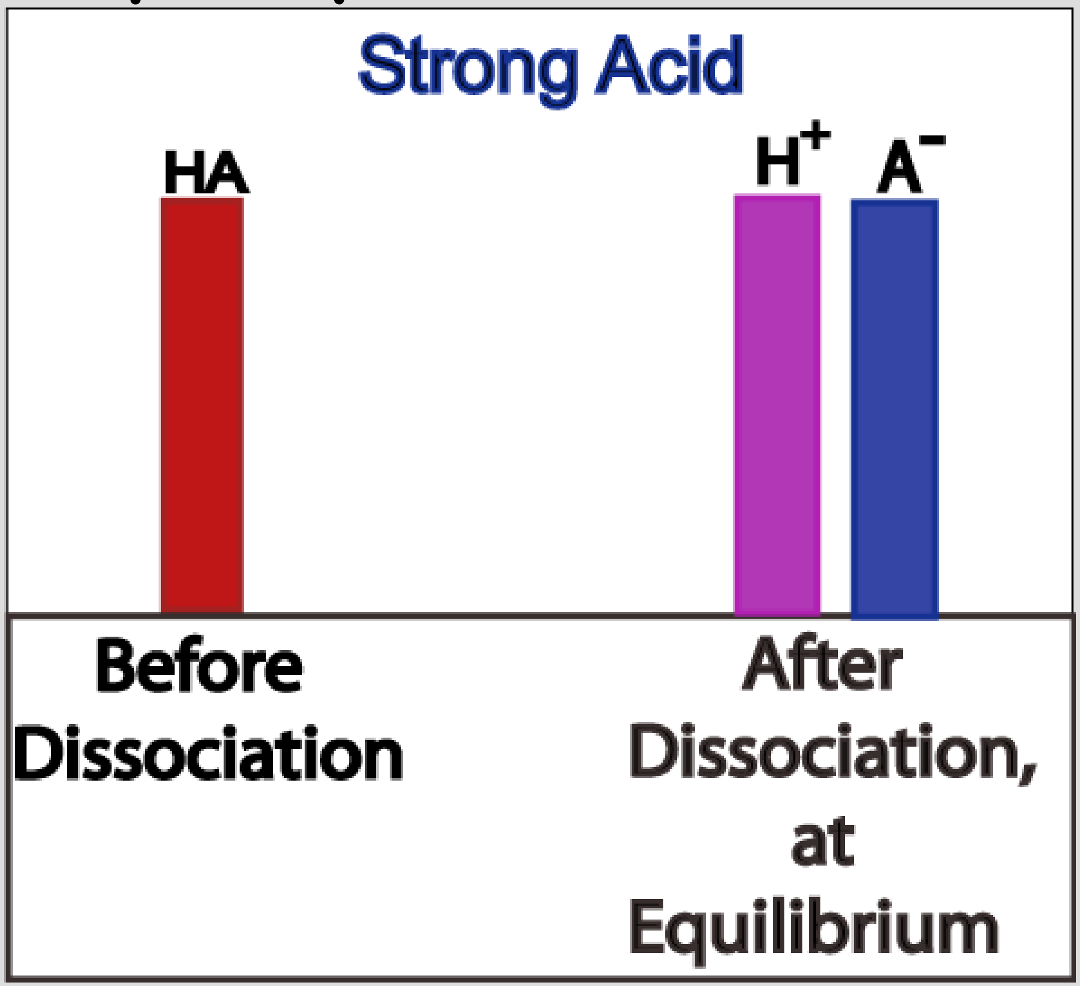
Acid | Proton | Conjugate base

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

Alternately, H^+ may be written in its hydrated form, H_3O^+ (hydronium ion)

Dissociation of Strong Acids

Strong acids are assumed to dissociate completely in solution.



Large K_a or small K_a?

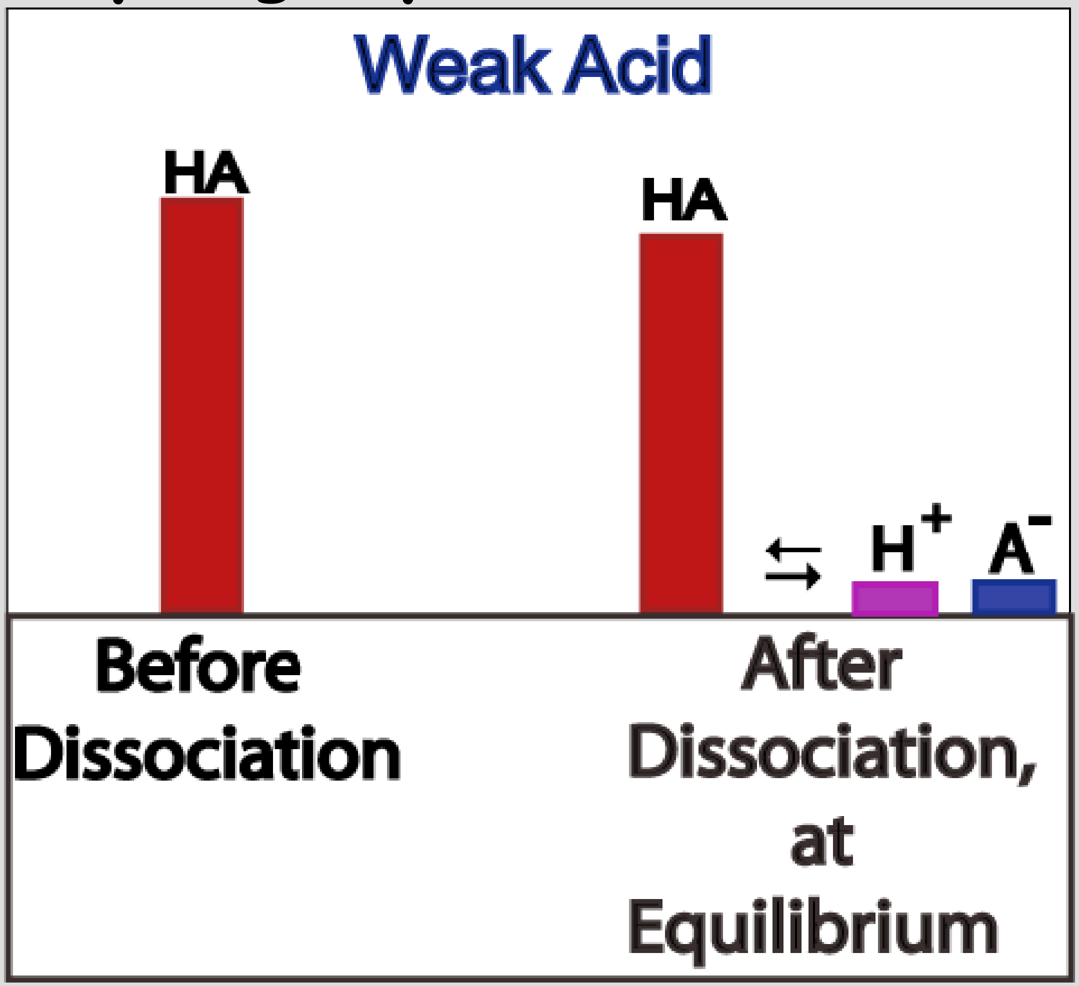
Reactant favored or product favored?

Dissociation Constants: Strong Acids

Acid	Formula	Conjugate Base	K_a
Perchloric	$HClO_4$	ClO_4^-	Very large
Hydriodic	HI	I^-	Very large
Hydrobromic	HBr	Br^-	Very large
Hydrochloric	HCl	Cl^-	Very large
Nitric	HNO_3	NO_3^-	Very large
Sulfuric	H_2SO_4	HSO_4^-	Very large
Hydronium ion	H_3O^+	H_2O	1.0

Dissociation of Weak Acids

Weak acids are assumed to dissociate only slightly (less than 5%) in solution.



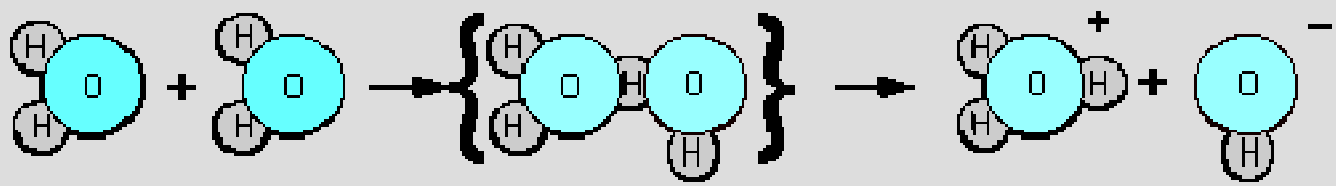
Large K_a or small K_a?

Reactant favored or product favored?

Dissociation Constants: Weak Acids

Acid	Formula	Conjugate Base	K_a
Iodic	HIO_3	IO_3^-	1.7×10^{-1}
Oxalic	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}
Sulfurous	H_2SO_3	HSO_3^-	1.5×10^{-2}
Phosphoric	H_3PO_4	$H_2PO_4^-$	7.5×10^{-3}
Citric	$H_3C_6H_5O_7$	$H_2C_6H_5O_7^-$	7.1×10^{-4}
Nitrous	HNO_2	NO_2^-	4.6×10^{-4}
Hydrofluoric	HF	F^-	3.5×10^{-4}
Formic	$HCOOH$	$HCOO^-$	1.8×10^{-4}
Benzoic	C_6H_5COOH	$C_6H_5COO^-$	6.5×10^{-5}
Acetic	CH_3COOH	CH_3COO^-	1.8×10^{-5}
Carbonic	H_2CO_3	HCO_3^-	4.3×10^{-7}
Hypochlorous	$HClO$	ClO^-	3.0×10^{-8}
Hydrocyanic	HCN	CN^-	4.9×10^{-10}

Self-Ionization of Water



$H_2O + H_2O \leftrightarrows H_3O^+ + OH^-$

At 25°, $[H_3O^+] = [OH^-] = 1 \times 10^{-7}$

<u>K_w is a constant at 25 °C:</u>

$$K_w = [H_3O^+][OH^-]$$

$$K_w = (1 \times 10^{-7})(1 \times 10^{-7}) = 1 \times 10^{-14}$$

Calculating pH, pOH

$$pH = -\log_{10}(H_3O^+)$$

$$pOH = -\log_{10}(OH^-)$$

Relationship between pH and pOH

$$pH + pOH = 14$$

Finding $[H_3O^+]$, $[OH^-]$ from pH, pOH

$$[H_3O^+] = 10^{-pH}$$

$$[OH^-] = 10^{-pOH}$$

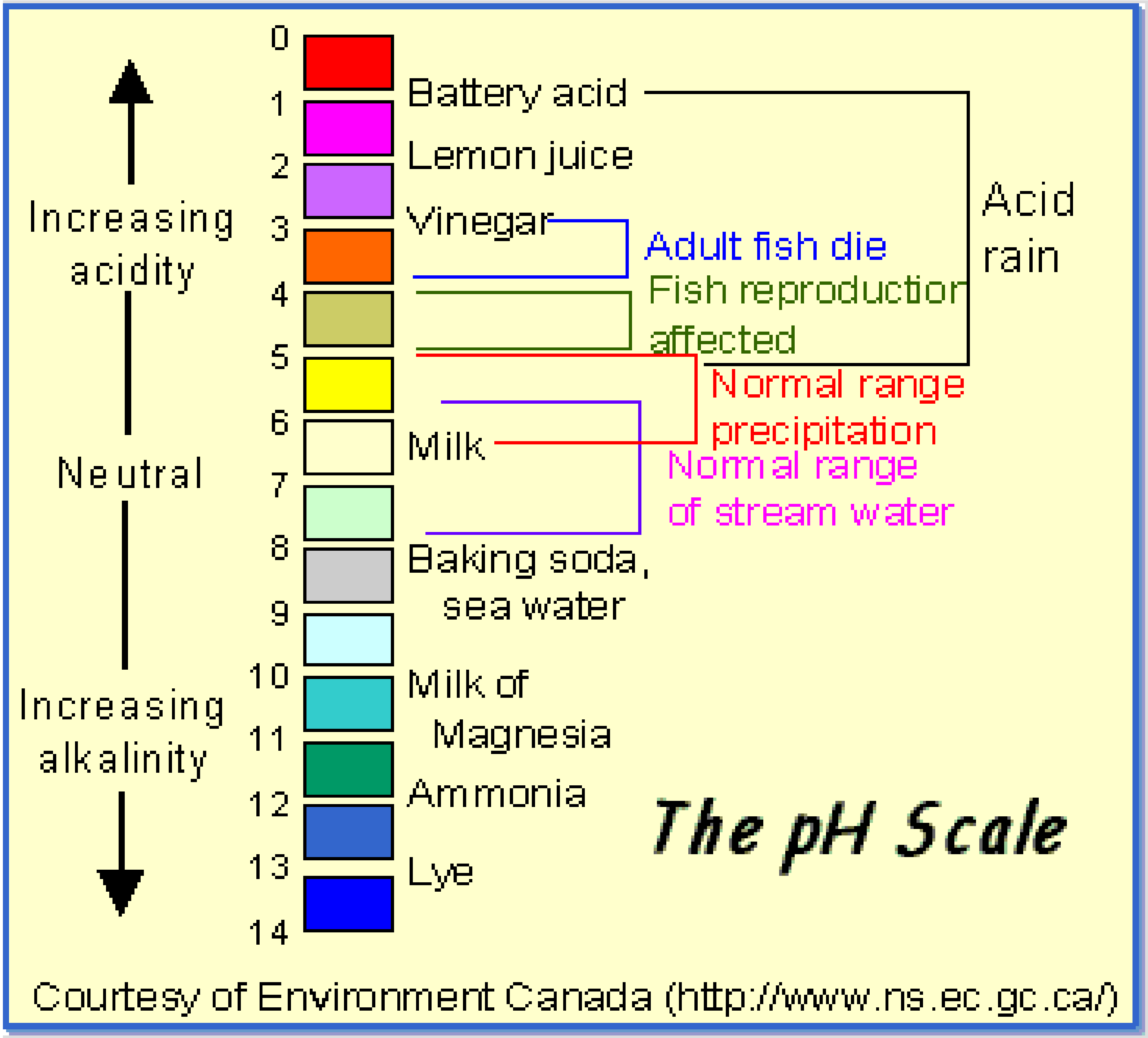
pH and pOH Calculations

$$\begin{tikzcd}[column sep=huge, row sep=huge]
H^+ \arrow[r, shift left, "{[OH^-] = \frac{1 \times 10^{-14}}{[H^+]}}"] \arrow[d, shift left, "{pH = -\log[H^+]}"] & OH^- \arrow[l, shift left, "{[H^+] = \frac{1 \times 10^{-14}}{[OH^-]}}"] \arrow[d, shift left, "{pOH = -\log[OH^-]}"] \\
pH \arrow[u, shift left, "{[H^+] = 10^{-pH}}"] \arrow[r, shift left, "{pOH = 14 - pH}"] & pOH \arrow[l, shift left, "{pH = 14 - pOH}"] \arrow[u, shift left, "{[OH^-] = 10^{-pOH}}"]
\end{tikzcd}$$

$$\mathbf{pH + pOH = 14}$$

$$\mathbf{Kw = [H^+]\,[OH^-] = 1 \times 10^{-14}}$$

pH Scale


0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
Increasing acidity
Neutral
Increasing alkalinity
Battery acid
Lemon juice
Vinegar
Milk
Baking soda, sea water
Milk of Magnesia
Ammonia
Lye
Adult fish die
Fish reproduction affected
Normal range precipitation
Normal range of stream water
Acid rain
The pH Scale
Courtesy of Environment Canada (http://www.ns.ec.gc.ca/)

A Weak Acid Equilibrium Problem

What is the pH of a 0.50 M solution of acetic acid, $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$?

Step #1: Write the dissociation equation

$$HC_2H_3O_2 \leftrightarrows H^+ + C_2H_3O_2^{-1}$$

A Weak Acid Equilibrium Problem

What is the pH of a 0.50 M solution of acetic acid, $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$?

Step #2: ICE it!

	$HC_2H_3O_2 \leftrightarrows$	H^+ +	$C_2H_3O_2^-$
I	0.50	0	0
C	- x	+x	+x
E	0.50 - x	x	x

A Weak Acid Equilibrium Problem

What is the pH of a 0.50 M solution of acetic acid, $HC_2H_3O_2$, K_a = 1.8 × 10^{-5} ?

Step #3: Set up the law of mass action

$$HC_2H_3O_2 \leftrightarrows H^+ + C_2H_3O_2^-$$

E	0.50 - x	x	x

$$1.8x10^{-5} = \frac{(x)(x)}{(0.50 - x)} \cong \frac{x^2}{(0.50)}$$

A Weak Acid Equilibrium Problem

What is the pH of a 0.50 M solution of acetic acid, $HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$?

Step #4: Solve for x, which is also $[H^+]$

$$HC_2H_3O_2 \leftrightarrows C_2H_3O_2^- + H^+$$

E	0.50 - x	x	x

$$1.8\,x10^{-5} = \frac{x^2}{(0.50)}$$

$[H^+] = 3.0 \text{ x } 10^{-3}$ M

$$pH = -\log(3.0\,x10^{3}) = 2.52$$

pK_a problem

- The pH of 0.015 M HNO_2 (nitrous acid) aqueous solution was measured to be 2.63. What is the value of Ka and pKa of nitrous acid?

$$[H_3O^+] = [NO_2^-] = 10^{-pH}$$

	HNO_2	$+ H_2O \rightleftharpoons$	H_3O^+	$+ NO_2^-$
I	0.015	–	0	0
C	$-x$	–	x	x
E	$0.015 - x$	–	x	x

$10^{-2.63} =$ 0.00234423 mol/L =x

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

$$pK_a = -\log(0.000434222) = 3.36229$$

Dissociation of Strong Bases

$$MOH(s) \rightarrow M^{+}(aq) + OH^{-}(aq)$$

- Strong bases are metallic hydroxides
  - Group I hydroxides (NaOH, KOH) are very soluble
  - Group II hydroxides (Ca, Ba, Mg, Sr) are less soluble
- pH of strong bases is calculated directly from the concentration of the base in solution

Reaction of Weak Bases with Water

The base reacts with water, producing its conjugate acid and hydroxide ion:

$CH_3NH_2 + H_2O \leftrightarrows CH_3NH_3^+ + OH^-$ $\quad K_b = 4.38 \times 10^{-4}$

$$K_b = 4.38 x 10^{-4} = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

K_b for Some Common Weak Bases

Many students struggle with identifying weak bases and their conjugate acids. What patterns do you see that may help you?

Base	**Formula**	**Conjugate Acid**	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	$CH_3NH_3^+$	4.38×10^{-4}
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	5.6×10^{-4}
Diethylamine	$(C_2H_5)_2NH$	$(C_2H_5)_2NH_2^+$	1.3×10^{-3}
Triethylamine	$(C_2H_5)_3N$	$(C_2H_5)_3NH^+$	4.0×10^{-4}
Hydroxylamine	$HONH_2$	$HONH_3^+$	1.1×10^{-8}
Hydrazine	H_2NNH_2	$H_2NNH_3^+$	3.0×10^{-6}
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	3.8×10^{-10}
Pyridine	C_5H_5N	$C_5H_5NH^+$	1.7×10^{-9}

A Weak Base Equilibrium Problem

What is the pH of a 0.50 M solution of ammonia, NH_3, $K_b = 1.8 \times 10^{-5}$?

Step #1: Write the equation for the reaction

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

A Weak Base Equilibrium Problem

What is the pH of a 0.50 M solution of ammonia, NH_3, $K_b = 1.8 \times 10^{-5}$?

Step #2: ICE it!

	NH_3 + H_2O	⇆	NH_4^+ +	OH^-
I	0.50		0	0
C	- x		+x	+x
E	0.50 - x		x	x

A Weak Base Equilibrium Problem

What is the pH of a 0.50 M solution of ammonia, NH_3, $K_b = 1.8 \times 10^{-5}$?

Step #3: Set up the law of mass action

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

	NH_3	H_2O	NH_4^+	OH^-
E	0.50 - x		x	x

$$1.8x10^{-5} = \frac{(x)(x)}{(0.50 - x)} \cong \frac{x^2}{(0.50)}$$

A Weak Base Equilibrium Problem

What is the pH of a 0.50 M solution of ammonia, NH_3, $K_b = 1.8 \times 10^{-5}$?

Step #4: Solve for x, which is also $[OH^-]$

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

E	0.50 - x	x	x

$$1.8\,x10^{-5} = \frac{x^2}{(0.50)}$$

$[OH^-] = 3.0 \times 10^{-3}$ M

A Weak Base Equilibrium Problem

What is the pH of a 0.50 M solution of ammonia, NH_3, $K_b = 1.8 \times 10^{-5}$?

Step #5: Convert $[OH^-]$ to pH

	$NH_3 + H_2O \leftrightarrows$	NH_4^+	$+ OH^-$
E	$0.50 - x$	x	x

$$pOH = -\log(3.0\,x\,10^{-3}) = 2.52$$

$$pH = 14.00 -\ pOH = 11.48$$

The pH of 0.1 M $C_4H_9NH_2(aq)$ (butylamine) aqueous solution was measured to be 12.04. What is the value of pK_b of butylamine?

$M = 0.1$ M $\qquad$ pH = 12.04

Analyzing the reaction with molarities,

	$C_4H_9NH_2$ +	$H_2O \rightleftharpoons$	$C_4H_9NH_3^+$ +	OH^-
I	0.1	–	0	0
C	$-x$	–	x	x
E	$0.1 - x$	–	x	x

$$K_b = \frac{[C_4H_9NH_3^+][OH^-]}{[C_4H_9NH_2]}$$

$$= \frac{x \quad x}{0.1 - x}$$

$$\text{pOH} = 14 - 12.04 = 1.96$$

$$[C_4H_9NH_3^+] = [OH^-] = 10^{-\text{pOH}}$$
$$= 10^{-1.96} = 0.0109648 \text{ mol/L}$$

$$K_b = \frac{(0.0109648)^2}{0.1 - 0.0109648}$$

$$K_b = 0.00135032$$

$$\text{p}K_b = -\log(0.00135032) = 2.86956$$

Calculate the pH of the solute in an aqueous solution of 0.0044 M codeine, if the pK_a of its conjugate acid is 8.21.

$$\begin{aligned} pK_b &= 14 - pK_a \\ &= 14 - 8.21 = 5.79 \\ K_b &= 10^{-5.79} = 1.62181 \times 10^{-6} \end{aligned}$$

codeine	$+ H_2O \rightleftharpoons$	codeine H^+	$+ OH^-$
0.0044	–	0	0
$-x$	–	$+x$	$+x$
$0.0044 - x$	–	x	x

$$K_b = \frac{[\text{codeine } H^+][OH^-]}{[\text{codeine}]} = 1.62181 \times 10^{-6} = \frac{x^2}{0.0044 - x} \approx \frac{x^2}{0.0044}$$

Assume x is small compared to 0.0044

$$\begin{aligned} x = [OH^-] &= \sqrt{0.0044(1.62181 \times 10^{-6})} \\ &= 8.44746 \times 10^{-5} \text{ mol/L}. \end{aligned}$$

$$pOH = -\log(8.44746 \times 10^{-5}) = 4.07327$$

$$pH = 14 - 4.07327 = 9.92673$$

What is the percentage protonation of the solute?

% protonation is the % of H^+ or OH^- that forms when the acid or base dissociates in water.

$[OH^-] = 8.44746 \times 10^{-5}$ mol/L $\quad$ $[\text{codeine}] = 0.0044$ mol/L

$$\%\ \text{protonation} = \frac{[OH^-]}{[\text{codeine}]} \times 100\% = \frac{8.44746 \times 10^{-5}}{0.0044} \times 100\%$$

$$= 1.91988\%$$

Acid-Base Properties of Salts

Type of Salt	Examples	Comment	pH of solution
Cation is from a strong base, anion from a strong acid	KCl, KNO_3 $NaCl$ $NaNO_3$	Both ions are neutral	Neutral

These salts simply dissociate in water:

$$KCl(s) \rightarrow K^+(aq) + Cl^-(aq)$$

Acid-Base Properties of Salts

Type of Salt	Examples	Comment	pH of solution
Cation is from a strong base, anion from a weak acid	$NaC_2H_3O_2$ KCN, NaF	Cation is neutral, Anion is basic	Basic

The basic anion can accept a proton from water:

$$\underset{base}{C_2H_3O_2^-} + \underset{acid}{H_2O} \leftrightarrows \underset{acid}{HC_2H_3O_2} + \underset{base}{OH^-}$$

Acid-Base Properties of Salts

Type of Salt	Examples	Comment	pH of solution
Cation is the conjugate acid of a weak base, anion is from a strong acid	NH_4Cl, NH_4NO_3	Cation is acidic, Anion is neutral	Acidic

The acidic cation can act as a proton donor:

$$NH_4^+(aq) \leftrightarrows NH_3(aq) + H^+(aq)$$

Acid — Conjugate base — Proton

Acid-Base Properties of Salts

Type of Salt	Examples	Comment	pH of solution
Cation is the conjugate acid of a weak base, anion is conjugate base of a weak acid	$NH_4C_2H_3O_2$ NH_4CN	Cation is acidic, Anion is basic	See below

- **IF K_a for the acidic ion is greater than K_b for the basic ion, the solution is acidic**
- **IF K_b for the basic ion is greater than K_a for the acidic ion, the solution is basic**
- **IF K_b for the basic ion is equal to K_a for the acidic ion, the solution is neutral**

Acid-Base Properties of Salts

Type of Salt	Examples	Comment	pH of solution
Cation is a highly charged metal ion; Anion is from strong acid	$Al(NO_3)_2$ $FeCl_3$	Hydrated cation acts as an acid; Anion is neutral	Acidic

Step #1:

$$AlCl_3(s) + 6H_2O \rightarrow Al(H_2O)_6^{3+}(aq) + Cl^-(aq)$$

Salt water Complex ion anion

Step #2:

$$Al(H_2O)_6^{3+}(aq) \rightarrow Al(OH)(H_2O)_5^{2+}(aq) + H^+(aq)$$

Acid Conjugate base Proton

- Nonmetallic oxides become acidic in water.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

- Metallic oxides become basic in water.

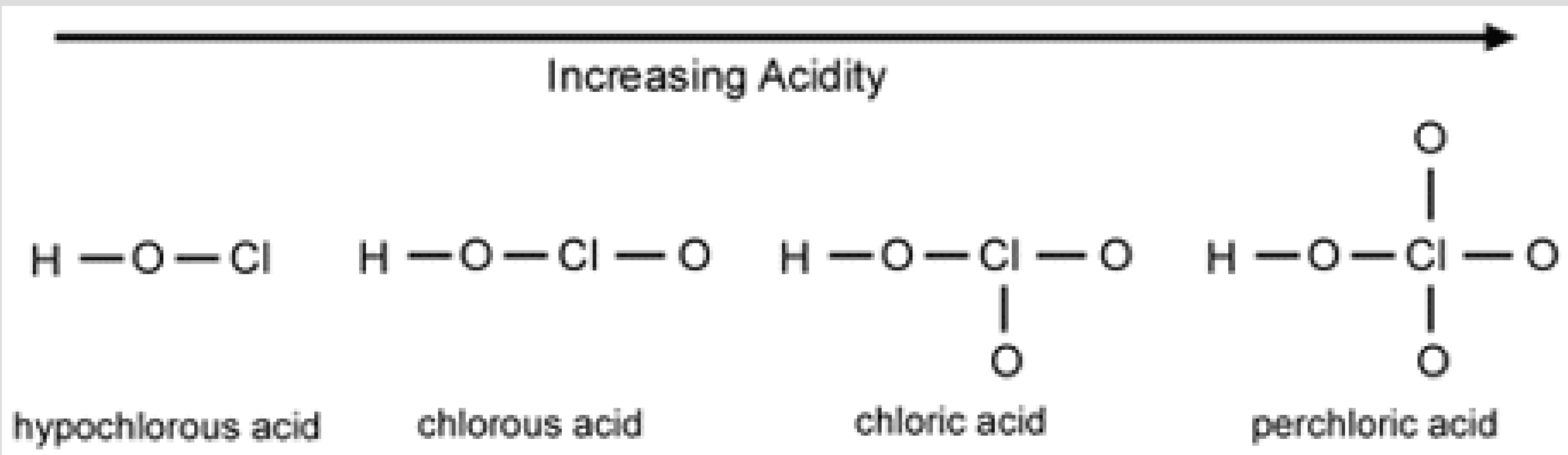
$$Na_2O \quad + \quad H_2O \quad \rightarrow \quad 2\ NaOH$$

- Amphoteric Substances
  - An **amphoteric oxide** is an oxide that is amphoteric, that is, it can act either as an acid or a base. In a strongly acidic environment, these oxides will act as bases; whereas in a strongly basic environment, these oxides will act as acids.
  - Examples:
  - Aluminum oxide
    - » in acid: $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$
    - » in base: $Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$

Oxide	Hydrated acid
Cl_2O_7	$HClO_4$
Cl_2O_5	$HClO_3$
Cl_2O_3	$HClO_2$
SO_3	H_2SO_4

Oxide	Hydrated base
MgO	$Mg(OH)_2$
ZnO	$Zn(OH)_2$
Fe_2O_3	$Fe(OH)_3$

Effect of Structure on Oxy-Acids



The more O’s, the stronger the acid and the lower the pH