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Chapter 15
Acids and Bases

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Arrhenius Definition

Arrhenius: any substance which ionizes in water to produce:
- Protons is an **Acid**.
- Hydroxide ions is a **Base**.

Better version of the Arrhenius definition:
Acid: Hydronium ions (H_3O^+) in water are acidic.
Base: Hydroxide ions (OH^-) in water are basic.

So, why is NH_3(aq) basic?

Brønsted-Lowry Concept

An alternative definition:

$\quad\quad$ **Brønsted-Lowry Acid** = Proton donor
$\quad\quad$ **Brønsted-Lowry Base** = Proton acceptor

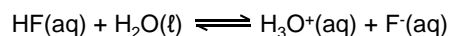Works for non-aqueous solutions and explains why NH_3 is basic:

$$NH_3(g) + H_2O(\ell) \longrightarrow NH_4^+(aq) + OH^-(aq)$$
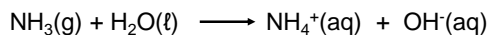
Base: H+ acceptor	Acid: H+ donor

Brønsted-Lowry Concept

Strong acids and bases almost completely ionize.

$$HNO_3(aq) + H_2O(\ell) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$
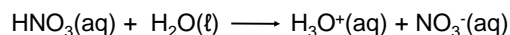
Weak acids and bases do not fully ionize.

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

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

Acid: H+ donor	Base: H+ acceptor	Acid: H+ donor	Base: H+ acceptor

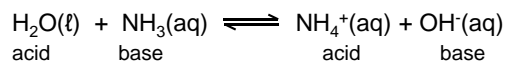Note: the products are a new acid and base pair.

Water's Role as Acid or Base

Water acts as a base when an acid dissolves in water:

$$\underset{\text{acid}}{HBr(aq)} + \underset{\text{base}}{H_2O(\ell)} \longrightarrow \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{Br^-(aq)}$$
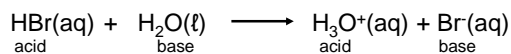
But water acts as an acid for some bases:

$$\underset{\text{acid}}{H_2O(\ell)} + \underset{\text{base}}{NH_3(aq)} \rightleftharpoons \underset{\text{acid}}{NH_4^+(aq)} + \underset{\text{base}}{OH^-(aq)}$$

Water is **amphiprotic** - it can donate or accept a proton (act as acid or base).

Conjugate Acid-Base Pairs

Molecules or ions related by the loss/gain of one H^+.

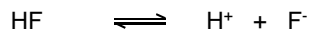| Conjugate Acid	Conjugate Base
H_3O^+	H_2O
CH_3COOH	CH_3COO^-
NH_4^+	NH_3
H_2SO_4	HSO_4^-
HSO_4^-	SO_4^{2-}
HCl	Cl^-

donate H+
accept H+

NH_4^+ and NH_2^- are **not** conjugate, conversion requires 2 H^+.

Conjugate Acid-Base Pairs

Identify the base conjugate to HF(aq) and the acid conjugate to HCO_3^-(aq).

$$HF \rightleftharpoons H^+ + F^-$$

Acid:
H$^+$ donor

Conjugate Base
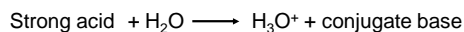
$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3$$
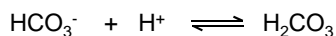
Base:
H$^+$ acceptor

Conjugate Acid

(CO_3^{2-} is the **base** conjugate to HCO_3^-)

Relative Strength of Acids & Bases

Strong acids are better H$^+$ donors than weak acids
Strong bases are better H$^+$ acceptors than weak bases
- Stronger acids have weaker conjugate bases.
- Weaker acids have stronger conjugate bases.

Strong acid + $H_2O \longrightarrow H_3O^+$ + conjugate base

Fully ionized, reverse reaction essentially does not occur.
The conjugate base is weak.

Weak acid + $H_2O \rightleftharpoons H_3O^+$ + conjugate base
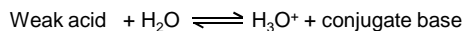
Weakly ionized, reverse reaction readily occurs.
The conjugate base is strong.

Relative Strength of Acids & Bases

	Conjugate acid	Conjugate base	
strong	H_2SO_4	HSO_4^-	extremely weak
	HBr	Br$^-$	
	HCl	Cl$^-$	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
	H_2SO_3	HSO_3^-	
	HSO_4^-	SO_4^{2-}	
	H_3PO_4	$H_2PO_4^-$	
	HF	F$^-$	
	CH_3COOH	CH_3COO^-	
	H_2S	HS$^-$	
	$H_2PO_4^-$	HPO_4^{2-}	
	NH_4^+	NH_3	
	HCO_3^-	CO_3^{2-}	
	H_2O	OH$^-$	
	OH$^-$	O^{2-}	
extremely weak	H_2	H$^-$	strong
	CH_4	CH_3^-	

Acid strength increasing →

Base strength increasing →

Relative Strength of Acids & Bases

Problem
Is the following aqueous reaction product or reactant favored?

$$NH_4^+ + F^- \rightleftharpoons NH_3 + HF$$
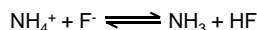
HF is a stronger acid than NH_4^+.
(NH_3 is a stronger base than F$^-$)

HF has greater tendency to ionize than NH_4^+.
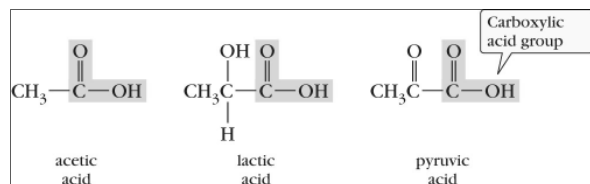(NH_3 more readily accepts H$^+$ than F$^-$)

Reactant Favored

Conj acid.	Conj. base
H_2SO_4	HSO_4^-
HBr	Br$^-$
HCl	Cl$^-$
┊	┊
HF	F$^-$
┊	┊
NH_4^+	NH_3
┊	┊
OH$^-$	O^{2-}
H_2	H$^-$
CH_4	CH_3^-

Acid strength increasing

Base strength increasing

Carboxylic Acids and Amines

Organic acids
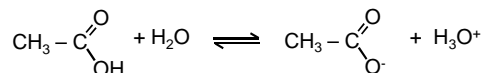Contain the carboxylic acid functional group:
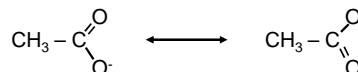

acetic acid   lactic acid   pyruvic acid

Carboxylic acid group

Carboxylic Acids and Amines

The carboxylic acid H is acidic (will ionize). All other protons are non acidic:

$$CH_3 - C{\overset{O}{\underset{OH}{}}} + H_2O \rightleftharpoons CH_3 - C{\overset{O}{\underset{O^-}{}}} + H_3O^+$$
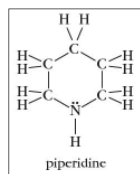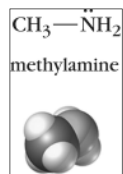
- O is very electronegative.
- O withdraws e$^-$ from the O–H bond (weakens O-H).
- Makes it easier for H$^+$ to leave.
- Once formed, the anion is stabilized by resonance:

$$CH_3 - C{\overset{O}{\underset{O^-}{}}} \longleftrightarrow CH_3 - C{\overset{O^-}{\underset{O}{}}}$$

Carboxylic Acids and Amines

Amine group: R–$\ddot{N}H_2$, R–$\ddot{N}HR$ or R–$\ddot{N}R_2$

- R = any hydrocarbon.
- Lone-pair on N accepts a proton (like NH_3).

CH_3—$\ddot{N}H_2$
methylamine

piperidine

Autoionization of Water

Two water molecules can react to form ions.
Autoionization occurs:

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

| Base | Acid | Acid | Base |
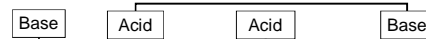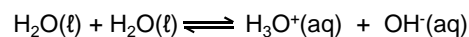
Heavily reactant favored.
Only a very small fraction is ionized:

ionization constant for water

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

$[H_2O]^2$ is omitted…

$\quad = (1.0 \times 10^{-7})(1.0 \times 10^{-7})$

$\quad = 1.0 \times 10^{-14} \quad$ (at 25°C)

Ionization Constant for Water

K_w, like all equilibrium constants, is T-dependent.
T = 25°C (77°F) is usually used as the standard T.

T (°C)	K_w
10	0.29×10^{-14}
15	0.45×10^{-14}
20	0.68×10^{-14}
25	1.01×10^{-14}
30	1.47×10^{-14}
50	5.48×10^{-14}

Autoionization of Water
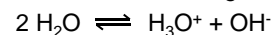
H_3O^+ and OH^- are present in all aqueous solutions.
Neutral solution.
   Pure water (@ 25°C): $[H_3O^+] = 10^{-7}$ M $= [OH^-]$

Acidic solution
If acid is added to water:

- [H_3O^+] is increased, disturbing the equilibrium:
$$2\, H_2O \rightleftharpoons H_3O^+ + OH^-$$
- Equilibrium shifts to remove $[H_3O^+]$ (and $[OH^-]$).
- Equilibrium is reestablished: [H_3O^+] $> 10^{-7}$ M $> [OH^-]$
- [H_3O^+][OH^-] $= K_w = 1.0 \times 10^{-14}$ at 25°C.

Autoionization of Water

Basic solution.
If base is added to water.

- Equilibrium shifts to remove [OH^-] (and $[H_3O^+]$).
- New equilibrium: $[H_3O^+] < 10^{-7}$ M $< [OH^-]$.
- [H_3O^+][OH^-] $= K_w = 1.0 \times 10^{-14}$ at 25°C.

Autoionization of Water

Example
Calculate the hydronium and hydroxide ion concentrations at 25°C in a 6.0 M aqueous sodium hydroxide solution.

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

NaOH (aq) is strong (100% ionized) so $[OH^-]$ = 6.0 M.

$\quad [H_3O^+](6.0) = 1.0 \times 10^{-14}$

$\quad [H_3O^+] = 1.7 \times 10^{-15}$ M   [OH^-] = 6.0 M

The pH scale

Acid concentration can vary over a very large range. A logarithmic scale is more convenient:

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

At 25°C a neutral aqueous solution has:
$$pH = -\log_{10}[1.0 \times 10^{-7}] = -(-7.00) = 7.00$$

Acidic solutions: pH < 7.00 (lower pH = more acidic).
Basic solutions: pH > 7.00 (higher pH = more basic).

The pH scale

Examples

Lemon juice: $[H_3O^+] = 1 \times 10^{-2}$ M $\boxed{\log_{10}(1 \times 10^{-x}) = -x}$
$$pH = -(-2.0) = 2.0$$

weak acid: $[H_3O^+] = 2.4 \times 10^{-5}$ M
$$pH = -(-4.62) = 4.62$$

2 sig. digits - digits after the decimal point are significant: "-4" is the power of 10 for the number (0.24×10^{-4}).

The pOH scale

Base concentrations:
$$pOH = -\log_{10}[OH^-]$$

A neutral solution (25°C) has:
$$pOH = -\log_{10}[1.0 \times 10^{-7}] = -(-7.00) = 7.00$$

Since $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$
$-\log(K_W) = -\log[H_3O^+] + (-\log[OH^-]) = -\log(1.0 \times 10^{-14})$

$$\boxed{pK_w = pH + pOH = 14.00}$$

(Valid in **all** aq. solns. at 25°C: acidic, neutral or basic)

pH Calculations

Given two aqueous solutions (25°C).
    Solution **A**: $[OH^-] = 4.3 \times 10^{-4}$ M,
    Solution **B**: $[H_3O^+] = 7.5 \times 10^{-9}$ M.
Which has the higher pH? Which is more acidic?

Solution **A**: $pOH = -\log[OH^-] = 3.37$
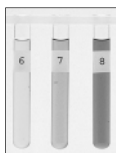 $pH + pOH = pK_w = 14.00$
                $pH = 10.63$

Solution **B**: $pH = -\log[H_3O^+] = 8.12$
        A has higher pH, **B** is more acidic

Measuring pH

H_3O^+ concentrations can be measured with an:
Electronic **pH meter**:
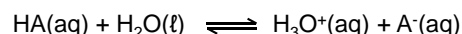• fast and accurate.
• preferred method.

Acid-base **Indicator**:
• substance changes color over a small pH range.
• may have multiple colors (e.g. bromthymol blue).
• one "color" may be colorless (e.g. phenolphthalein).
• cheap and convenient.

Ionization Constants of Acids and Bases

When an acid ionizes in water:

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

The **acid ionization constant** is used to report the degree of ionization:
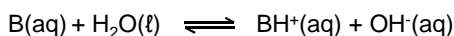
$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \qquad \text{(Water omitted, as usual)}$$

Strong acids have large K_a values.
Weak acid have small K_a values.

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Base Ionization Constants

For a base in water:

$$B(aq) + H_2O(\ell) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

The base ionization constant, K_b, is:

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

If the base is an anion:

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

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

Values of Acid and Base Ionization Constants

See Table 15.2: ionization constants for common acids and their conjugate bases.

Strong acid K_a are hard to measure.
• They are very large, ≈100% ionized.
• Assume they are fully ionized.
• Larger K_a = stronger acid.

Strong base K_b are hard to measure…
• Larger K_b = stronger base.

K_a Values for Polyprotic Acids
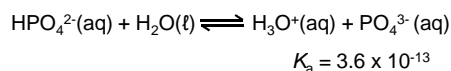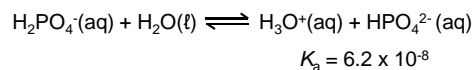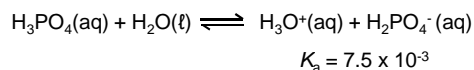
Some acids can donate more than one H^+:

Formula	Name	Acidic H's
H_2S	Hydrosulfuric Acid	2
H_3PO_4	Phosphoric Acid	3
H_2CO_3	Carbonic Acid	2
HOOC-COOH	Oxalic acid	2
$C_3H_5(COOH)_3$	Citric acid	3

Each H^+ ionization has a different K_a.
• The 1st proton is easiest to remove.
• The 2nd is harder, etc.

K_a Values for Polyprotic Acids

Phosphoric acid (H_3PO_4) has three acidic protons:

$$H_3PO_4(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$
$$K_a = 7.5 \times 10^{-3}$$

$$H_2PO_4^-(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$
$$K_a = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$
$$K_a = 3.6 \times 10^{-13}$$

H^+ harder to remove

Molecular Structure and Acid Strength

What makes a strong acid?
• A weak H–A bond, so H^+ can be easily removed!

Consider the binary acids HF, HCl, HBr, HI.

HX		Bond Energy (kJ)	K_a
HF	weak acid	566	7×10^{-4}
HCl		431	1×10^7
HBr	strong acids	366	1×10^8
HI		299	1×10^{10}

smaller bond energy
larger acid strength

Strength of Oxoacids

H-O-Z

Acid		Bonding	EN_Z	K_a
hypochlorous acid	HClO	H-O-Cl	3.0	4×10^{-8}
hypobromous acid	HBrO	H-O-Br	2.8	3×10^{-9}
hypoiodous acid	HIO	H-O-I	2.5	2×10^{-11}

Weaker H-O bond … Stronger acid.

If Z is electronegative it will pull e^- to it: H–O–Z

Larger EN_Z = weaker bond (stronger acid).

Strength of Oxoacids

H-O-Z   with Z = group of atoms.

Acid		Bonding	K_a
perchloric acid	$HClO_4$	H-O-ClO$_3$	1×10^8
chloric acid	$HClO_3$	H-O-ClO$_2$	1×10^3
chlorous acid	$HClO_2$	H-O-ClO	1×10^{-2}
hypochlorous acid	HClO	H-O-Cl	4×10^{-8}

Stronger acid = weaker H-O bond.

If Z is:

   More e$^-$ withdrawing = weaker bond = stronger acid.

   More O atoms = more e$^-$ withdrawing.

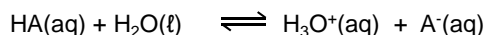## Problem Solving Using K_a and K_b

Example: K_a from pH

Lactic acid is monoprotic. The pH of a 0.100 M solution was 2.43 at 25°C. Determine K_a for this acid.
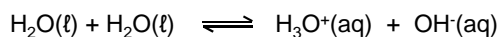
Using the pH information:

- log [H_3O^+] = 2.43   [H_3O^+] = $10^{-2.43}$ = 0.0037 M

These hydronium ions are produced by:

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

and from the autoionization of water:

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

Problem Solving Using K_a and K_b

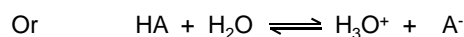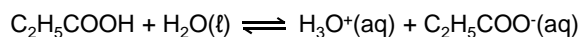|	$HA(aq) + H_2O(\ell) \rightleftharpoons$	$H_3O^+(aq) +$	$A^-(aq)$
[ ]$_{initial}$	0.100	1.0×10^{-7} (water autoionization)	0
[ ]$_{change}$	-0.0037	+0.0037	+0.0037
[ ]$_{equil}$	0.100 – 0.0037	0.0037*	0.0037

*Ignore the water contribution because it is so small.

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

$= \dfrac{(0.0037)(0.0037)}{(0.100 - 0.0037)} = 1.4 \times 10^{-4}$

Problem Solving Using K_a and K_b

Example: pH from K_a

Determine the pH of a 0.100 M propanoic acid solution at 25°C. $K_a = 1.4 \times 10^{-5}$. What % of acid is ionized?

$C_2H_5COOH + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + C_2H_5COO^-(aq)$

Or $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

$K_a = \dfrac{[H_3O^+][A^-]}{[HA]} = 1.4 \times 10^{-5}$

Problem Solving Using K_a and K_b

Determine the pH of 0.001 M propanoic acid soln. at 25°C. K_a = 1.4 x10^{-5}. What % of acid is ionized?

	$HA(aq) + H_2O(\ell) \rightleftharpoons$	$H_3O^+(aq) +$	$A^-(aq)$
[ ]$_{initial}$	0.100	0*	0
[ ]$_{change}$	-x	+x	+x
[ ]$_{equil}$	0.100 – x	x*	x

*Ignore the water contribution

$K_a = 1.4 \times 10^{-5} = \dfrac{[H_3O^+][A^-]}{[HA]} = \dfrac{x^2}{(0.100 - x)} \approx \dfrac{x^2}{0.100}$

x << 0.1 (K_a is very small)

Problem Solving Using K_a and K_b

$1.4 \times 10^{-5} \approx \dfrac{x^2}{0.100}$

$x = \sqrt{(1.4 \times 10^{-5})(0.100)} = 0.00118$ M

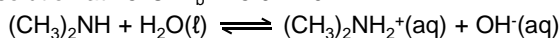(x << 0.100 M; the approximation is good)

pH = -log(0.00118) = 2.93

%-ionized = $\left(\dfrac{x}{0.100} \right) 100\% = 1.18 \%$

Problem Solving Using K_a and K_b

Determine [OH$^-$] and pH of a 0.060 M dimethylamine solution at 25°C. K_b = 5.9 x 10^{-4}.

$(CH_3)_2NH + H_2O(\ell) \rightleftharpoons (CH_3)_2NH_2{}^+(aq) + OH^-(aq)$

	B(aq) + H$_2$O(l) $\rightleftharpoons$ BH$^+$(aq) + OH$^-$(aq)		
[ ]$_{initial}$	0.060	0	0*
[ ]$_{change}$	-x	+x	+x
[ ]$_{equilib}$	0.060 – x	x	x*

*Ignore water.

K_b = 5.9 x 10^{-4} = $\dfrac{[BH^+][OH^-]}{[B]}$

$= \dfrac{x^2}{(0.060 - x)} \approx \dfrac{x^2}{0.060}$

Problem Solving Using K_a and K_b

$x = \sqrt{(5.9 \times 10^{-4})(0.060)} = 0.0059 \text{ M} = [OH^-]$

pOH = 2.23   pH = 14.00 – 2.23 = 11.77

x ≈ [B]/10, the approximation of x << [B] is marginal…

Problem Solving Using K_a and K_b

Check the exact solution.

$5.90 \times 10^{-4} = \dfrac{x^2}{0.060 - x}$

$x^2 = (5.90 \times 10^{-4})(0.060 - x)$

$x^2 + 5.90 \times 10^{-4}\,x - 3.54 \times 10^{-5} = 0$

Quadratic solution: x = 0.0057 M

pOH = 2.25   pH = 11.75

The approximate method gave pOH = 2.23

In general, approx. method is "good" if x < [ ]/20

Relationship between K_a and K_b values

For an acid-base conjugate pair: HA and A$^-$

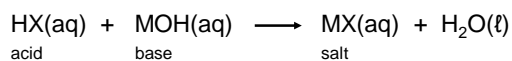$K_a \times K_b = \dfrac{[H_3O^+][A^-]}{[HA]}\,\dfrac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w$

Phenol, C_6H_5OH, is a weak acid, K_a = 1.3 x 10^{-10} at 25°C. Calculate K_b for the phenolate ion $C_6H_5O^-$.

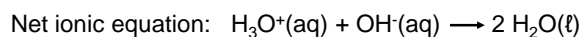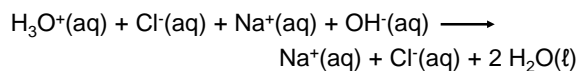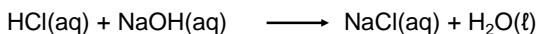$K_a \times K_b = 1.0 \times 10^{-14}$

$K_b = \dfrac{1.0 \times 10^{-14}}{1.3 \times 10^{-10}} = 7.7 \times 10^{-5}$

Acid Base Reactions of Salts

Salt = ionic compound formed in acid + base reaction.

$\underset{\text{acid}}{HX(aq)} + \underset{\text{base}}{MOH(aq)} \longrightarrow \underset{\text{salt}}{MX(aq)} + H_2O(\ell)$

Strong acid + strong base:

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(\ell)$

$H_3O^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow$
$\qquad\qquad Na^+(aq) + Cl^-(aq) + 2\,H_2O(\ell)$

Net ionic equation: $H_3O^+(aq) + OH^-(aq) \longrightarrow 2\,H_2O(\ell)$

Salts of Strong Bases and Strong Acids

$H_3O^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell) + H_2O(\ell)$
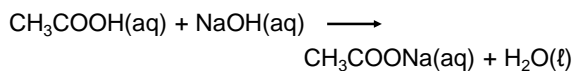
Acid   Base   Base   Acid
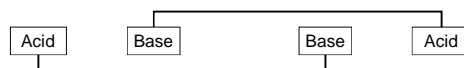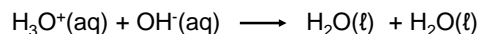
- Na$^+$ and Cl$^-$ are spectators – appear as reactants and products.
- Net products are water: weak acid *and* weak base.
- Final solution has pH = 7.

Strong acid + strong base → salt and water.

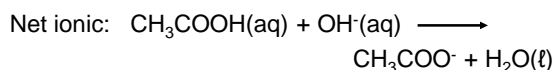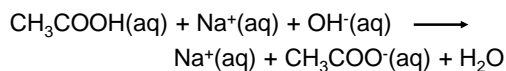Equal moles generate a neutral solution.

Salts of Strong Bases and Weak Acids

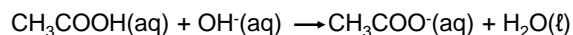Weak acid + strong base is more complex.

$CH_3COOH(aq) + NaOH(aq) \longrightarrow$
$$CH_3COONa(aq) + H_2O(\ell)$$

Weak acids partially ionize in solution.
• Do not dissociate the acid on the reactant side.

$CH_3COOH(aq) + Na^+(aq) + OH^-(aq) \longrightarrow$
$$Na^+(aq) + CH_3COO^-(aq) + H_2O$$

Net ionic: $CH_3COOH(aq) + OH^-(aq) \longrightarrow$
$$CH_3COO^- + H_2O(\ell)$$

Salts of Strong Bases and Weak Acids

$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(\ell)$

| Acid | Base | Base | Acid |

Acetate ions form:
• acetate is a weak base (much stronger than water).
• solution is basic (pH > 7.0).

$CH_3COO^-(aq) + H_2O(\ell) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$
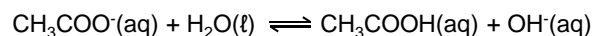
A **hydrolysis** reaction – water is broken apart.

Salts of Strong Bases and Weak Acids

For a weak acid + strong base, pH depends on K_b.
Larger K_b = stronger base

Example What is the pH of 1.50 M $Na_2CO_3(aq)$?
$K_b (CO_3^{2-}) = 2.1 \times 10^{-4}$.

Na^+ is the conjugate acid of NaOH (strong base).
• It remains 100% ionized.
• Na^+ has no effect on pH.
CO_3^{2-} is the conjugate base of HCO_3^- (weak acid).
• Hydrolysis: $CO_3^{2-} + H_2O \rightarrow HCO_3^-$ and OH^-
• Changes the pH.

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pH of a Salt Solution

What is the pH of a 1.50 M $Na_2CO_3(aq)$? $K_b = 2.1 \times 10^{-4}$

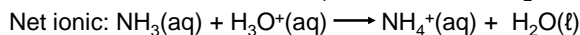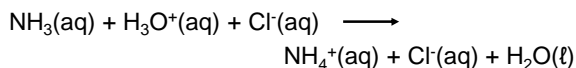|	$CO_3^{2-}(aq) + H_2O(\ell) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$		
[ ]$_{initial}$	1.50	0	0
[ ]$_{change}$	- x	+x	+x
[ ]$_{equil}$	1.50 - x	x	x

$$K_b = 2.1 \times 10^{-4} = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{x^2}{(1.50 - x)} \approx \frac{x^2}{1.50}$$

$x = 1.77 \times 10^{-2}$ $pOH = -\log(1.77 \times 10^{-2}) = 1.75$
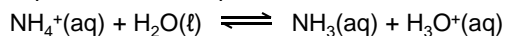$$pH = 14.00 - 1.75 = 12.25$$

Salts of Weak Bases and Strong Acids

Similar arguments.
$NH_3(aq) + HCl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$

$NH_3(aq) + H_3O^+(aq) + Cl^-(aq) \longrightarrow$
$$NH_4^+(aq) + Cl^-(aq) + H_2O(\ell)$$
Net ionic: $NH_3(aq) + H_3O^+(aq) \longrightarrow NH_4^+(aq) + H_2O(\ell)$

An equimolar reaction produces an acidic solution:
$NH_4^+(aq) + H_2O(\ell) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

The final pH depends on K_a:
Larger K_a = more acidic

---

pH of a Salt Solution

Find the pH of 0.132 M $NH_4Br(aq)$. Is this solution acidic, basic or neutral? $K_a(NH_4^+) = 5.6 \times 10^{-10}$.

The solution contains NH_4^+ ions and Br^- ions.
• NH_4^+ is the conjugate acid of NH_3 (a weak base).
  ▪ $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$
  ▪ Acidic solution!

• Br^- is the conjugate base of HBr (a strong acid).
  ▪ Br^- ions stay fully ionized.
  ▪ Does not change the pH.

pH of a Salt Solution

pH of 0.132 M NH_4Br? Acidic, basic or neutral? $K_a(NH_4^+) = 5.6 \times 10^{-10}$.

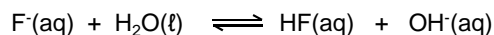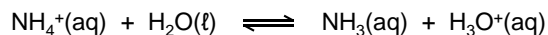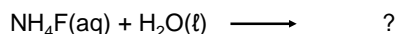|	$NH_4^+(aq) + H_2O(\ell) \rightleftharpoons NH_3(aq) +$		$H_3O^+(aq)$
[ ]$_{initial}$	0.132	0	0
[ ]$_{change}$	- x	+x	+x
[ ]$_{equil}$	0.132 - x	x	x

$$K_a = 5.6 \times 10^{-10} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = \frac{x^2}{(0.132 - x)} \approx \frac{x^2}{0.132}$$

$x = 8.57 \times 10^{-6}$ pH $= -\log(8.57 \times 10^{-6}) = 5.07$

Acidic!

Salts of Weak Bases and Weak Acids

The most difficult. Consider qualitative results. e.g.

$NH_4F(aq) + H_2O(\ell) \longrightarrow$　　　　?

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

$F^-(aq) + H_2O(\ell) \rightleftharpoons HF(aq) + OH^-(aq)$

$K_a(NH_4^+) = 5.6 \times 10^{-10}$; $K_b(F^-) = 1.4 \times 10^{-11}$

K_a (weak acid) $> K_b$ (weak base)

The ammonium reaction is more favorable.

The solution will be acidic!

Acids, Bases and Salts

Strong acid + strong base $\rightarrow$ salt solution, pH = 7

Strong acid + weak base $\rightarrow$ salt solution, pH < 7

Weak acid + strong base $\rightarrow$ salt solution, pH > 7

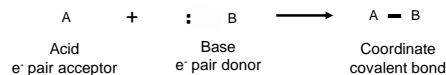Weak acid + weak base $\rightarrow$ salt solution, pH = ?
　　　Need K's　　　　　　"strongest wins"

Lewis Acids and Bases

The most general acid-base definition:

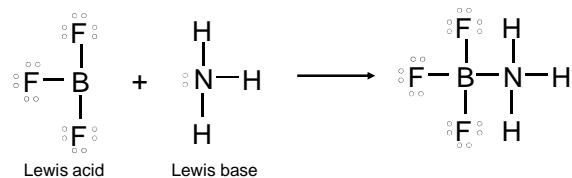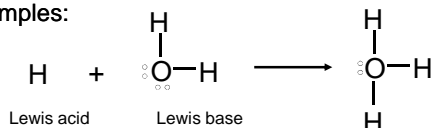A **Lewis acid** accepts a pair of e$^-$ to form a bond.
A **Lewis base** donates a pair of e$^-$ to form a bond.

A	+	: B	$\longrightarrow$	A — B
Acid		Base		Coordinate
e$^-$ pair acceptor		e$^-$ pair donor		covalent bond

Coordinate covalent bond: a shared e$^-$ pair, with both e$^-$ donated by the same atom.

Lewis Acids and Bases
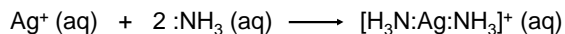
Examples:

H^+ + H_2O $\longrightarrow$ H_3O^+

Positive Metal Ions as Lewis Acids

Metal ions can act as Lewis acids. They have:
• Missing e$^-$.
• Empty valence orbitals.
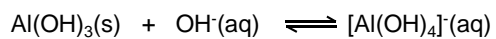• Metal ion + Lewis base $\rightarrow$ complex ion

$Ag^+ (aq)$ + $2\ :NH_3 (aq)$ $\longrightarrow$ $[H_3N:Ag:NH_3]^+ (aq)$

Hydroxide ions are Lewis bases.
• O is e$^-$ rich (has large electronegativity): $[\overset{\delta-}{:\ddot{O}}-\overset{\delta+}{H}]^-$
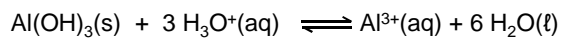• Can easily donate an e$^-$ pair to a bond.

Positive Metal Ions as Lewis Acids

Many metal hydroxides are **amphoteric** – they react with acids and bases.
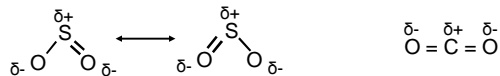
Aluminum hydroxide can act as a Lewis acid:

$$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons [Al(OH)_4]^-(aq)$$

or as a Brønsted-Lowry base:

$$Al(OH)_3(s) + 3 H_3O^+(aq) \rightleftharpoons Al^{3+}(aq) + 6 H_2O(\ell)$$

Neutral Molecules as Lewis Acids

Non-metal oxides act as Lewis acids.
- O attracts e^- from any multiple bond.
- Leaves the other non-metal e^- deficient.

- Susceptible to attack by Lewis base: