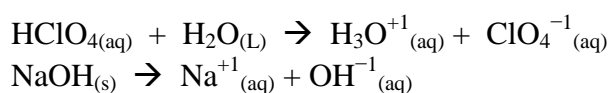


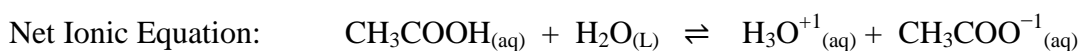
Ch 15 Acids Bases (OpenStax Sections [14.1](#), [14.2](#), and [14.3](#))

Svante Arrhenius Concept (1884)

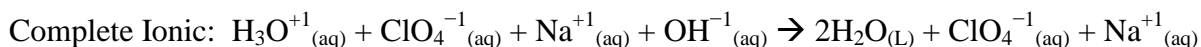
- An **acid** is a substance that, when **dissolved in H<sub>2</sub>O**, increases the concentration of the hydronium ion, **H<sub>3</sub>O<sup>+1</sup><sub>(aq)</sub>**. H<sub>3</sub>O<sup>+1</sup> is equivalent to an H<sup>+1</sup> attached to H<sub>2</sub>O.
- A **base** is a substance that, when **dissolved in H<sub>2</sub>O**, increases the concentration of the hydroxide ion, **OH<sup>-1</sup><sub>(aq)</sub>**. OH<sup>-1</sup> is equivalent to an H<sub>2</sub>O that lost an H<sup>+1</sup>.
- [Strong acids and bases](#) are those that **completely dissociate** in water. These reactions go to completion, leaving practically no reactant. **Their K<sub>c</sub>'s are very large.**



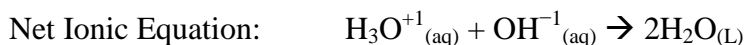
- **Weak acids and bases** are **not** completely ionized in water. Their reactions are **reversible** and have **finite K<sub>c</sub>'s** that are less than 1. The left side of their net chemical equation with water is favored. They exist primarily as the **aqueous molecules**, not as the ions.



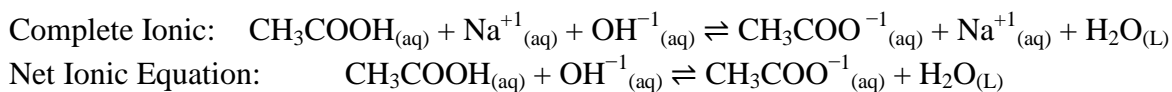
- Neutralization of strong acid and strong base always involves a reaction of H<sub>3</sub>O<sup>+1</sup> and OH<sup>-1</sup>.



- The reaction between **a strong acid and a strong base** always has the **same** enthalpy. The reaction is exothermic with **ΔH = - 55.90 kJ per mole of H<sub>3</sub>O<sup>+1</sup>**. This occurs because the net ionic equation (see [pages 2 and 3](#)) is always the **same**.



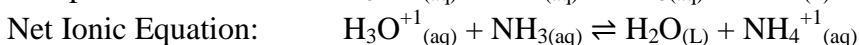
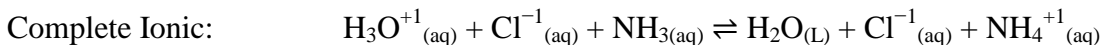
- Reactions involving **weak acids or bases** do not give the same net ionic equation. This is because they exist primarily as **aqueous molecules**, not ions. Weak acids and bases **do not cancel out** of the net chemical equations.



- The Arrhenius concept is limited because it pertains only to aqueous ionic solutions. Modern concepts include acid-base reactions that do not involve H<sub>3</sub>O<sup>+1</sup><sub>(aq)</sub> or OH<sup>-1</sup><sub>(aq)</sub>.

Brønsted-Lowry (Danish and British) Concept (1923)

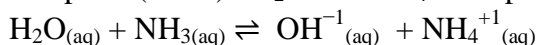
- An **acid** is a **proton ( $\text{H}^+$ ) donor**, and a **base** is a **proton acceptor** in a **proton transfer reaction**.
- This can be seen with the aqueous reaction between HCl and  $\text{NH}_3$ , where  $\text{H}_3\text{O}^+$  is the proton donor (acid),  $\text{NH}_3$  is the proton acceptor (base), and  $\text{OH}^-$  is not involved.



- HCl and  $\text{NH}_3$  will also react together in an organic solvent such as benzene. HCl and  $\text{NH}_3$  are the acid and base. No  $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$ , or  $\text{H}_2\text{O}$  molecules are involved.



- In a reversible acid-base rxn, both forward and reverse reactions involve proton transfers. Both directions are acid-base reactions and both sides contain both an acid and a base.  $\text{NH}_3$  and  $\text{OH}^-$  are proton acceptors (bases).  $\text{H}_2\text{O}$  and  $\text{NH}_4^+$  are proton donors (acids).



- $\text{NH}_3$  and  $\text{NH}_4^+$  are a **conjugate acid-base pair**.

That is, they are two species that differ only by the gain or loss of **one proton**.

$\text{NH}_4^+$  is the conjugate acid cation of  $\text{NH}_3$ .

One of the two conjugates is on each side of the proton transfer reaction.

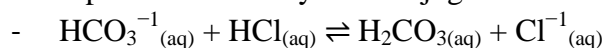
An acid-base reaction contains [two pairs of conjugates](#), such as  $\text{NH}_3/\text{NH}_4^+$  and  $\text{H}_2\text{O}/\text{OH}^-$ .

- **Amphiprotic** species can **either** gain or lose a proton, and can act as either an acid or a base, depending on the other reactant.  $\text{HCO}_3^-$  (Example 15.01) and  $\text{H}_2\text{O}$  are both amphiprotic.
- **Amphoteric** is a more general term for a substance that can act as either an acid or a base, but **may or may not** possess a proton.  $\text{Zn}(\text{OH})_{2(\text{s})}$  is one example (in chapter 17).  $\text{Zn}(\text{OH})_{2(\text{s})}$  can react with  $\text{OH}^-$  to become  $\text{Zn}(\text{OH})_4^{2-}_{(\text{aq})}$  or with  $\text{H}^+$  to become  $\text{Zn}^{2+}_{(\text{aq})}$ .

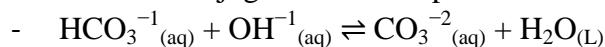
Brønsted-Lowry concept has a greater scope than the Arrhenius definition:

1. A base is a species that accepts  $\text{H}^+$ .  
( $\text{OH}^-$  is only one example,  $\text{NH}_3$  is another.)
2. Acids and bases can be ions, as well as molecular substances.  
( $\text{NH}_4^+$  is an acid and  $\text{CH}_3\text{COO}^-$  is a base.)
3. Acid-base reactions are not restricted to aqueous solutions.  
(HCl/ $\text{NH}_3$  in benzene or in vapor phase does not involve  $\text{H}_2\text{O}$ ,  $\text{H}_3\text{O}^+$ , or  $\text{OH}^-$ .)
4. Some species can be either acid or base.  
( $\text{HCO}_3^-$  and  $\text{H}_2\text{O}$  are both amphiprotic.)

Example 15.01 Identify the Conjugate Acid-Base Pairs



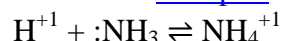
The two conjugate acid/base pairs are  $\text{H}_2\text{CO}_3 / \text{HCO}_3^-$  and  $\text{HCl} / \text{Cl}^-$ .



The two conjugate acid/base pairs are  $\text{HCO}_3^- / \text{CO}_3^{2-}$  and  $\text{H}_2\text{O} / \text{OH}^-$ .

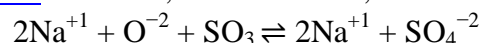
### Gilbert N. Lewis Concept (1923)

- A **Lewis acid** is a species that can form a covalent bond by **accepting an e<sup>-1</sup> pair**.
- A **Lewis base** is a species that can form a covalent bond by **donating an e<sup>-1</sup> pair**.
- NH<sub>3</sub> reacts with H<sup>+1</sup> because N has a **lone pair** and H<sup>+1</sup> has an empty 1s orbital.

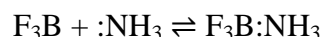


- Another example would be the reaction between Na<sub>2</sub>O<sub>(s)</sub> and SO<sub>3(g)</sub>.

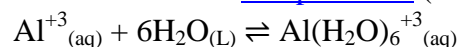
Review the [Lewis structures](#) for oxide, sulfur trioxide, and sulfate.



- A Lewis acid-base reaction creates a new **coordinate covalent bond**.



- The Lewis theory explains the formation of **complex ions** (coordination chemistry).



Water is a ligand, which is a Lewis base.

It donates an e<sup>-1</sup> pair to a metal cation, which is a Lewis acid.

- The Lewis theory explains many reactions, like those above, that we may not ordinarily think of as acid-base reactions.

### Acid & Base Strength (from Brønsted-Lowry concept)

- Stronger acids lose protons more easily than weaker acids.
- Stronger bases accept protons more strongly than weaker bases.
- HCl + H<sub>2</sub>O → Cl<sup>-1</sup> + H<sub>3</sub>O<sup>+1</sup> goes to completion, HCl readily gives up its H<sup>+1</sup> to H<sub>2</sub>O. The reaction goes from **stronger acid to weaker acid**, so HCl is a stronger acid than H<sub>3</sub>O<sup>+1</sup>.

- CH<sub>3</sub>COOH + H<sub>2</sub>O ⇌ CH<sub>3</sub>COO<sup>-1</sup> + H<sub>3</sub>O<sup>+1</sup>

Dissociation is 1%. CH<sub>3</sub>COOH is a weaker acid than H<sub>3</sub>O<sup>+1</sup>.

- HF + H<sub>2</sub>O ⇌ F<sup>-1</sup> + H<sub>3</sub>O<sup>+1</sup>

Dissociation is 3%. HF is a weaker acid than H<sub>3</sub>O<sup>+1</sup>, but stronger than CH<sub>3</sub>COOH.

- Order of Acidity: HCl > H<sub>3</sub>O<sup>+1</sup> > HF > CH<sub>3</sub>COOH

- Reverse of CH<sub>3</sub>COOH reaction goes to 99% completion, while reverse of HCl reaction does not happen appreciably at all.

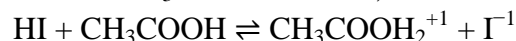
So, the **strongest acids** have the **weakest conjugate bases**, and **vice-versa**.

- Order of Basicity: CH<sub>3</sub>COO<sup>-1</sup> > F<sup>-1</sup> > H<sub>2</sub>O > Cl<sup>-1</sup>

The reactions go from **stronger base to weaker base**.

- The reactions always favor going from **stronger acid/base to weaker acid/base**.
- Any strong acid in H<sub>2</sub>O is converted completely to H<sub>3</sub>O<sup>+1</sup>. So H<sub>3</sub>O<sup>+1</sup> is the strongest acid that can exist in H<sub>2</sub>O. This is called **leveling**, and a weaker base than H<sub>2</sub>O, such as CH<sub>3</sub>COOH, is needed as a solvent to see a difference between two strong acids.
- If HCl and HI are each placed in separate CH<sub>3</sub>COOH solutions, then CH<sub>3</sub>COOH acts as a base and accepts an H<sup>+1</sup> from the acid.

HI is ionized more so than HCl in CH<sub>3</sub>COOH solution, and is therefore the stronger acid.



- [Figure 14.8](#) predicts the favored directions (from stronger to weaker) of acid-base reactions. The top left of the table has the strongest acids, and acids get weaker going down the column. The bottom right of the table has strongest bases, and bases get weaker going up the column.

Example 15.03 Predict the favored direction for  $\text{SO}_4^{-2} + \text{HF} \rightleftharpoons \text{HSO}_4^{-1} + \text{F}^{-1}$

- The left side is favored: weaker base + weaker acid  $\rightleftharpoons$  stronger acid + stronger base

### Strength of **Binary Acids** ( $\text{H}_n\text{X}$ )

- The strength trends are functions of bond strength (within a periodic table column) and bond polarity (across a row in the table).

### Bond Strength

- The **larger** atom X is, the **weaker** the bond strength is. As a result, the  $\text{H}^{+1}$  is held less tightly, and the acid strength is **greater**.
- Atoms get larger going down a column in the periodic table. So, binary halogen acids (column VIII-A) are strongest at the bottom of the table:  

$$\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$$

### Bond Polarity

- For acid HX, H is  $\delta+$  and X is  $\delta-$ . The more **polarized** the bond is, the more **easily** the  $\text{H}^{+1}$  is removed, and the **greater** the acid strength.
- Going across a row (left to right), atoms get smaller, but only slowly and not enough to create an acid strength trend.
- However, **electronegativity increases** enough across a row for both polarity and acid strength to increase:  $\text{H}_2\text{O} < \text{HF}$  and  $\text{H}_2\text{S} < \text{HCl}$

### Molecular Structure and Strength of **Oxoacids** ( $\text{H-O-Y}$ and $\text{H-O-YO}_n$ )

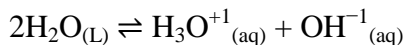
- Bond polarity determines acid strength for HOY. So, acid strength depends on the **e/n of Y** because the size and e/n of O is constant.  $\text{HOI} < \text{HOBr} < \text{HOCl}$  because Cl has highest electronegativity.
- $(\text{HO})_m\text{YO}_n$  **polarity increases with n** so  $\text{HOCl} < \text{HOClO} < \text{HOClO}_2 < \text{HOClO}_3$ . Increasing the number of free O's makes the anion more  $\delta-$  and the H more  $\delta+$ . So the H-O bond is more polarized and more acidic.

### Polyprotic acids (more than one $\text{H}^{+1}$ )

- Removing an  $\text{H}^{+1}$  makes an anion with a negative charge. The negative charge of the anion is attracted to the positive charge of  $\text{H}^{+1}$ .
- So, the **anion** is a **weaker** acid than the neutral compound:  $\text{HSO}_4^{-1} < \text{H}_2\text{SO}_4$

## Self-Ionization of Water

- Water does transfer an  $H^+$  from one molecule to another.



$H_2O$  is a pure liquid, so it is omitted from the equilibrium constant expression.

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \text{ (at } 25^\circ C\text{)}$$

- In **neutral** water,  $[H_3O^+] = [OH^-] = 10^{-7.00}$  and  $pH = 7.00$
- If an acid or base is added to water, neither  $[H_3O^+]$ , nor  $[OH^-]$ , is  $10^{-7}$ .

However  $K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$  **still** applies.

- For 0.10 M HCl,  $[H_3O^+] = 0.10 = 10^{-1.0}$  and  $pH = 1.0$ .

So,  $[OH^-] = K_w \div [H_3O^+] = 10^{-14} \div 0.10 = 1.0 \times 10^{-13}$ .

- For 0.010 M NaOH,  $[OH^-] = 0.010 = 10^{-2.0}$ .

So,  $[H_3O^+] = K_w \div [OH^-] = 10^{-14} \div 10^{-2.0} = 1.0 \times 10^{-12}$  and  $pH = 12.0$ .

In **acidic** solution:  $[H_3O^+] > 10^{-7}$  and  $[OH^-] < 10^{-7}$

In **neutral** solution:  $[H_3O^+] = [OH^-] = 10^{-7}$

In **basic** solution:  $[H_3O^+] < 10^{-7}$  and  $[OH^-] > 10^{-7}$

Example 15.04 a. 0.36 M  $HNO_3$  (strong acid)

$$[H_3O^+] = 0.36 \text{ M}$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{10^{-14}}{0.36} = 2.8 \times 10^{-14} \text{ M}$$

b. 0.020 M  $Ca(OH)_2$  (strong base)

$$[OH^-] = 2 \times 0.020 \text{ M} = 0.040 \text{ M}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.040} = 2.5 \times 10^{-13} \text{ M}$$

pH, pOH, and  $pK_w$

- **pH** =  $-\log_{10}[H_3O^+]$  (decimal places + 1 = number of significant digits)

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

For  $[H_3O^+] = 0.0010 = 10^{-3.0}$ , we have  $pH = -\log(10^{-3.0}) = -(-3.0) = +3.0$

- Similarly, **pOH** =  $-\log_{10}[OH^-]$  and  $[OH^-] = 10^{-pOH}$

- Also,  **$pK_w$**  =  $-\log_{10}[K_w] = -\log(10^{-14.00}) = -(-14.00) = +14.00$

- $K_w = [H_3O^+][OH^-] = 10^{-14.00}$ , so  **$pK_w = pH + pOH = 14.00$**

Example 15.05

$$[H_3O^+] = 1.80 \times 10^{-4} \text{ M} \quad pH = -\log(1.80 \times 10^{-4}) = 3.74$$

$$pOH = 14.00 - 3.74 = 10.26 \quad [OH^-] = 10^{-10.26} = 5.50 \times 10^{-11} \text{ M}$$

Example 15.06

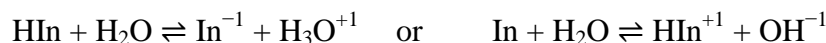
$$pH = 7.35 \quad [H_3O^+] = 10^{-7.35} = 4.47 \times 10^{-8} \text{ M}$$

$$pOH = 14.00 - 7.35 = 6.65 \quad [OH^-] = 10^{-6.65} = 2.24 \times 10^{-7} \text{ M}$$

pH Indicators

- **pH Indicators** are a pair of weak acid/base conjugates where either only one conjugate has a color or each conjugate has a different color.

- The indicator has a reversible reaction:



- For phenolphthalein:  $H_2In + 2OH^- \rightleftharpoons In^{2-} + 2H_2O$

$H_2In$  is colorless, and **pink**  $In^{2-}$  forms at  $pH > 8.2$ .

### Acid-Base Theories

Theory	Acid	Base
Arrhenius	Creates $[\text{H}_3\text{O}^{+1}_{(\text{aq})}]$	Creates $[\text{OH}^{-1}_{(\text{aq})}]$
Brønsted –Lowry	Donates $\text{H}^{+1}$	Accepts $\text{H}^{+1}$
Lewis	Accepts $2e^{-1}$	Donates $2e^{-1}$

### pH/pOH Ranges and Hydronium/Hydroxide Concentration Ranges for Acidic and Basic Solutions

	Acid	Neutral	Base
$[\text{H}_3\text{O}^{+1}]$	$> 10^{-7}$	$1.00 \times 10^{-7}$	$< 10^{-7}$
pH	$< 7$	7.00	$> 7$
$[\text{OH}^{-1}]$	$< 10^{-7}$	$1.00 \times 10^{-7}$	$> 10^{-7}$
pOH	$> 7$	7.00	$< 7$