Bases = Anti-Acids

Example:
$$HCI(aq) + H_2O(I) \rightarrow H_3O^+(aq) + CI^-(aq)$$

$$NaOH(aq) \rightarrow Na^{+}(aq) + OH^{-}(aq)$$

$$H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(I)$$

Net:
$$HCI(aq) + NaOH(aq) \rightarrow Na^{+}(aq) + CI^{-}(aq) + H_2O(I)$$

The process is called **neutralization** (neither acidic nor basic)

How much hydronium ion is in a neutral solution?

$$[H_3O^+][OH^-]=1x10^{-14}$$
 at 25°C $2H_2O \rightleftharpoons H_3O^+ + OH^-$

Concentration in Molar (M) of hydronium ion times the concentration in Molar (M) of hydroxide ion is a constant in water solution.

If [H₃O⁺] goes up, [OH⁻] goes down; if [OH⁻] goes up [H₃O⁺] goes down.

In a neutral solution $[H_3O^+] = [OH^-] = 1x10^{-7}$

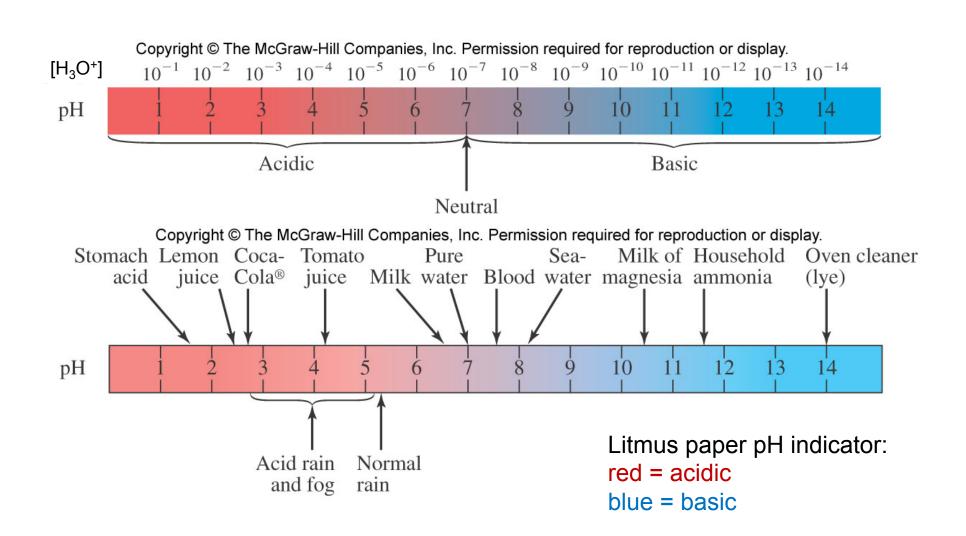
if
$$[H_3O^+] > [OH^-]$$
 acidic solution: if $[H_3O^+] = 1x10^{-4}$ then $[OH^-] = 1x10^{-10}$ acidic if $[H_3O^+] < [OH^-]$ basic solution: if $[H_3O^+] = 1x10^{-9}$ then $[OH^-] = 1x10^{-5}$ basic

$[H3O^{+}]/[OH^{-}]/pH/pOH$

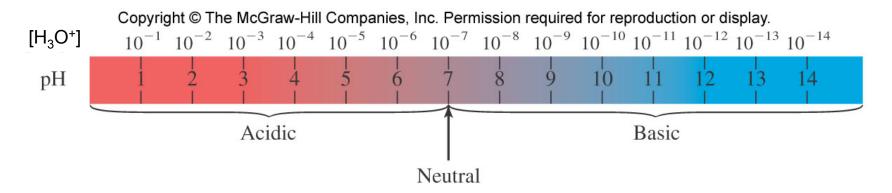
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[H_3O^+] \times [OH^-] = 1 \times 10^{-14} (a constant)
definition of pH: pH = -\log[H_3O^+] H_3O^+ = 10^{-pH}
pH<7 acidic pH>7 basic pH=7 neutral
[H_3O^+] > [OH^-] [H_3O^+] < [OH^-] [H_3O^+] = [OH^-]
pOH = -log[OH^{-}]
                             pH+pOH=14
If [H_3O^+] = 1 \times 10^{-3} then [OH^-] = ??? 1 x 10<sup>-11</sup> acidic?
If [H_3O^+] = 1 \times 10^{-8} then [OH^-] = ??? 1 \times 10^{-6} acidic? no
If [OH^{-}] = 1 \times 10^{-5} then [H_3O^{+}] = ??? 1 x 10<sup>-9</sup> acidic? no
If [OH^{-}] = 1 \times 10^{-10} then [H_3O^{+}] = ??? 1 \times 10^{-4} acidic? yes
If pH=5 then pOH=??? 9
                                 acidic?
                                             yes
If pH=7 then pOH=??? 7
                                 acidic?
                                             no
If pH=8 then pOH=??? 6
                                  acidic?
                                             no
If pOH=3 then pH=??? 11
                                 acidic?
                                             no
```

pH of Common Substances

lower pH \rightarrow higher [H₃O⁺] \rightarrow more acidic



pH of Rain, Normal and Otherwise...



Rain condenses from water vapor in the atmosphere...so atmospheric gases will be dissolved in the water:

An **equilibrium** is established between carbon dioxide and water:

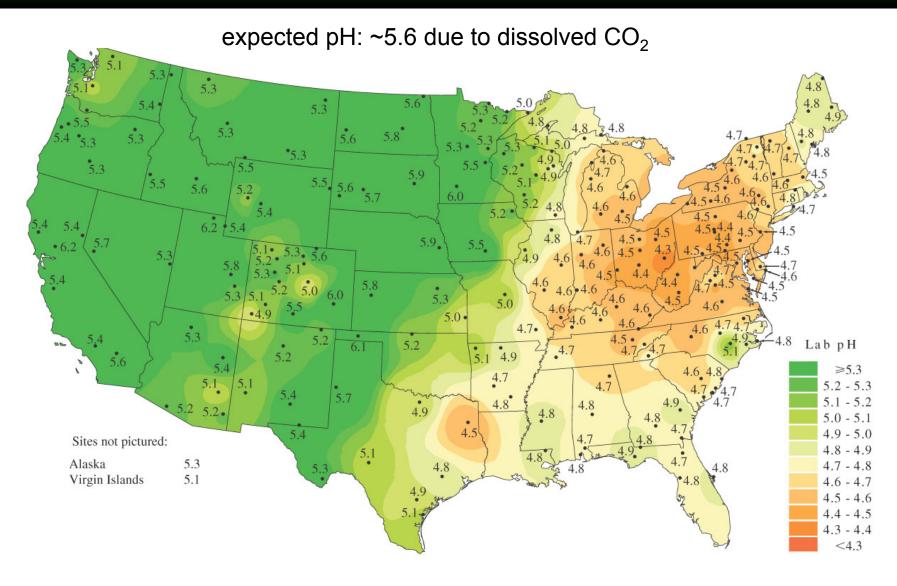
$$CO_2 + H_2O \longrightarrow H_2CO_3$$
 $HO \longrightarrow C \longrightarrow OF$

$$H_2CO_3 + H_2O \implies H_3O^+ + HCO_3^-$$

$$HCO_{3}^{-} + H_{2}O \implies H_{3}O^{+} + CO_{3}^{2-}$$

...this leads to a pH 5.6 solution

pH of US Rain (2005)



Where does extra acidity come from?

Sources of "Extra" Acidity

Remember: SO₂ is formed when coal is burned

$$SO_2(g) + H_2O(I) \rightarrow H_2SO_3(aq)$$
 Sulfurous acid $H_2SO_3(aq) + H_2O(I) \rightarrow H_3O^+(aq) + HSO_3^-(aq)$

$$SO_3(g) + H_2O(I) \rightarrow H_2SO_4(aq)$$
 Sulfuric acid $H_2SO_4(aq) + H_2O(I) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$ hydrogen sulfate ion $HSO_4^-(aq) + H_2O(I) \rightarrow H_3O^+(aq) + SO_4^{2-}(aq)$ sulfate ion

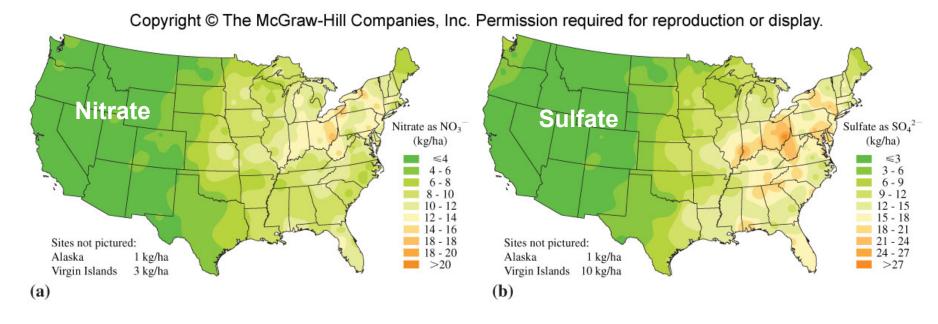
Remember: NO₂ formed when any combustion occurs (from N₂ in air)

$$4NO_2(g) + 2H_2O(I) + O_2(g) \rightarrow 4HNO_3(aq)$$
 Nitric acid
 $HNO_3(aq) + H_2O(I) \rightarrow H_3O^+(aq) + NO_3^-(aq)$ nitrate ion

Deposition of Nitrate and Sulfate

Dry deposition—solid (pollutant) particles dispersed in the atmosphere, eventually settle back to the ground

Wet deposition—solid particles dissolved in rain, return to the ground via precipitation



Burning coal (Chapter 4):

$$2C_{135}H_{96}O_9NS + 313O_2 \rightarrow 270CO_2 + 96H_2O + 2NO_2 + 2SO_2$$

In atmosphere: $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

SO₄²⁻ and NO₃⁻ from coal combustion; NO₃⁻ also from automobile traffic

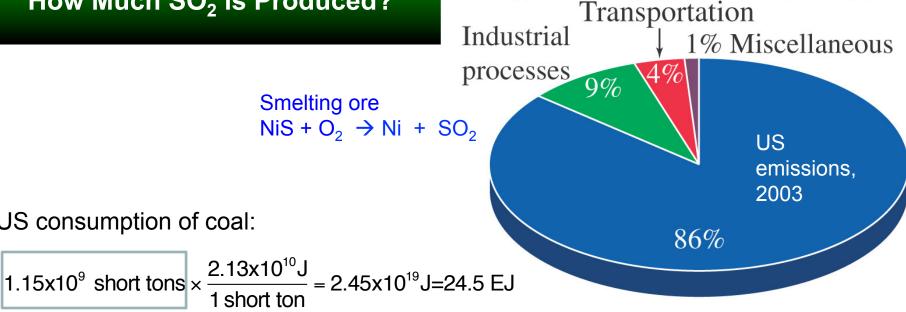
How Much SO₂ is Produced?

US consumption of coal:

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Fuel Combustion

burning coal



SO₂ generation from coal combustion (assumes no mitigation):

$$2C_{135}H_{96}O_9NS + 313O_2 \rightarrow 270CO_2 + 96H_2O + 2NO_2 + 2SO_2$$

Molar mass: $C_{135}H_{96}O_9NS$: 135x12.0 +96x1.0+9x16.0+14.0+32.1=1906.1 g/mol

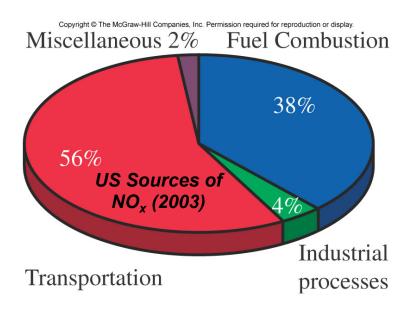
$$1.15x10^9 \text{ short ton} \times \frac{907.2 \text{ kg}}{1 \text{ short ton}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mole Coal}}{1906.1 \text{ g Coal}} \times \frac{1 \text{ mole SO}_2}{1 \text{ mole Coal}} \times \frac{64.1 \text{ g SO}_2}{1 \text{ mole SO}_2} = 3.51x10^{13} \text{ g SO}_2$$

 $= 3.9 \times 10^7$ short ton assumes no mitigation

Acid Rain, West Coast Style

Very little SO₂ in Los Angeles, nevertheless the rain can be very acidic...

In Unit 2.2: Nitrogen (N₂) not very reactive but is 78% of air and does react at high temperatures



2NO + $O_2 \rightarrow 2NO_2$ slow in air but accelerated by VOC (volatile organic compounds) & OH

VOC + OH
$$^{\bullet} \rightarrow A$$

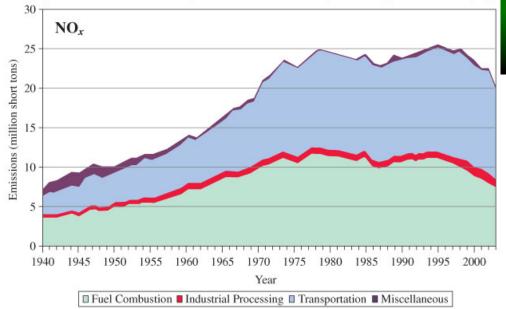
 $A + O_2 \rightarrow A'$
 $A' + NO \rightarrow A'' + NO_2$

A, A', and A" produced from oxidation of VOC

$$NO_{2}(g) + OH^{*}(g) \rightarrow HNO_{3}(g)$$

 $HNO_{3}(g) + H_{2}O(I) \rightarrow H_{3}O^{+}(aq) + NO_{3}^{-}(aq)$

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SO₂ 30 25 25 10 1940 1945 1950 1955 1960 1965 1970 1975 1980 1985 1990 1995 2000 Year Fuel Combustion Industrial Processing Transportation Miscellaneous

US Emissions of SO_x and NO_x

1940-2003
Emissions in millions of short tons

More difficult to estimate emissions of NO_x than SO_x (less centralized emission points for the former)

Note: for SO_2 , we estimated 39 million short tons... (?)

1970s: catalytic converters introduced (S removed from gasoline)

1990: Clean air act amendments

(a)

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Table 6.1 Estimated Global Emissions of Sulfur Dioxide and Nitrogen Oxides				
	SO ₂ *	NO_x^{\dagger}		
Natural Sources				
Oceans [‡]	25			
Soil		5.6		
Volcanoes	10			
Lightning		5.0		
Subtotal	35	10.6		
Anthropogenic Sources				
All sources	69			
Fossil-fuel combustion	Note we estimated 35x10 ⁹ kg for	33.0		
Biomass combustion	US without emission controls	7.1		
Aircraft		0.7		
Subtotal	69	40.8		
Total in billions of kg	104	51.4		

^{*}In units of 10¹² g sulfur/year.

Source: Climate Change 2001: The Scientific Basis, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, 2001, p. 315 and p. 260. Reprinted with permission.

[†]In units of 10¹² g nitrogen/year.

^{*}Sulfur is emitted from oceans in the form of dimethyl sulfide rather than SO₂. This compound is naturally converted to sulfur dioxide by the hydroxyl radical, • OH.

Impacts of Acid Rain

$$4Fe(s) + 2O_2(g) + 8H_3O^+(aq) \rightarrow 4Fe^{2+}(aq) + 12H_2O(l)$$

 $4Fe^{2+}(aq) + O_2(g) + 12H_2O(l) \rightarrow 2Fe_2O_3(s) + 8H_3O^+(aq)$ acid is

Net: $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ rust

catalytic



Impacts of Acid Rain

$$CaCO_3(s) + 2H_3O^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + 3H_2O(l)$$

Marble contains both magnesium carbonate and calcium carbonate

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In 1944 © NYC Parks Photo Archive/Fundamental Photographs



At present
© Kristen Brochmann/Fundamental Photographs

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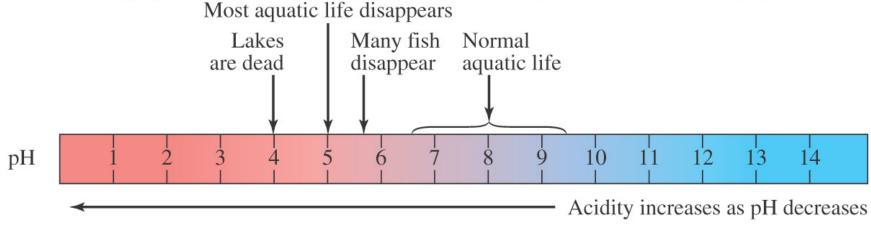
Effects of Acid Rain and Recovery Benefits

Effects of Acid Kain and Recovery Benefits				
Effects	Recovery Benefits			
Materials Acid deposition contributes to the corrosion and deterioration of buildings, cultural objects, and cars. This decreases their value and increases the cost of correcting and repairing damage.	Less damage to buildings, cultural objects, and cars, thus lowering the future costs of correcting and repairing such damage. See Section 6.10.			
Human Health Sulfur dioxide and nitrogen oxides in the air increase deaths from asthma and bronchitis and impair the cardiovascular system.	Fewer visits to the emergency room, fewer hospital admissions, and fewer deaths. See Section 6.11.			
Visibility In the atmosphere, sulfur dioxide and nitrogen oxides form sulfate and nitrate aerosols that impair visibility and affect enjoyment of national parks and other scenic views.	Reduced haze, therefore the ability to view scenery at a greater distance and with greater clarity. See Section 6.11.			
Surface Waters Acidic surface waters decrease the survivability of animal life in lakes and streams. In more severe instances, acidity eliminates some or all types of fish and organisms.	Lower levels of acidity in the surface waters and a restoration of animal life in the more severely damaged lakes and streams. See Section 6.13.			
Forests Acid deposition contributes to forest degradation by impairing the growth of trees and increasing their susceptibility to winter injury, insect infestation, and drought. It also causes leaching and depletion of natural nutrients in forest soil.	Less stress on trees, thereby reducing the effects of winter injury, insect infestation, and drought. Less leaching of nutrients from soil, thereby improving the overall forest health.			

Source: Adapted from *Emission Trends and Effects in the Eastern U.S.*, United States General Accounting Office, Report to Congressional Requesters, March, 2000.

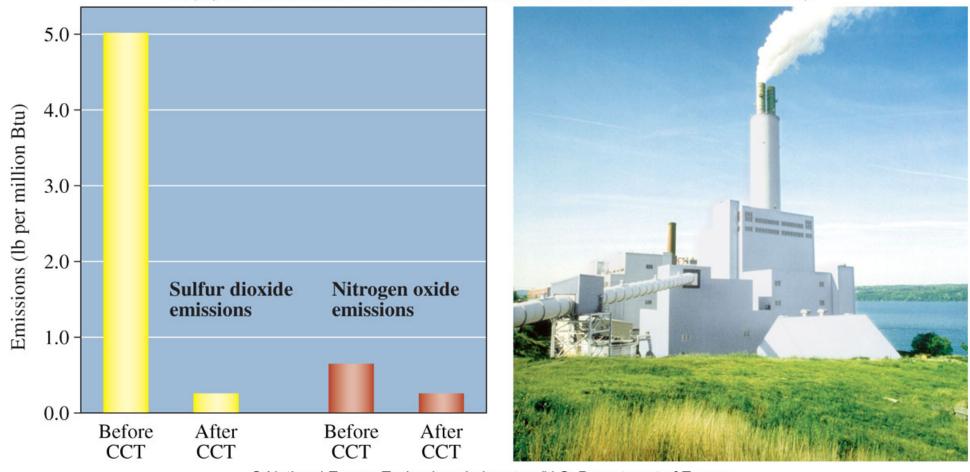
Environmental/Biological Effects of Acidification

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SO_x and NO_x Reduction via Clean Coal Technology





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CCT: clean coal technology

Review

Summary

- Composition of the atmosphere is pretty vital to life
 - Components are mostly pretty simple gases in ppt-pph concentrations
 - N₂, O₂, Ar, CO₂
 - Pollutants are found in ppb-ppm concentrations
 - criteria (regulated) pollutants: CO, NO₂, O₃, SO₂, Pb, PM_x
 - CO₂ is not a pollutant
 - direct (out of the "tailpipe") versus indirect pollutants
- Knowledge of chemical nomenclature important
 - forms of matter (especially compounds vs mixtures)
 - prefixes for naming compounds (N₂O is not the same thing as NO₂!)
- Balancing chemical reactions leads to insight on fighting pollution
 - e.g. complete vs incomplete combustion
 - e.g. catalytic conversion of CO to CO₂
- Pollutants can be reduced, but never removed entirely
 - balancing the costs against the benefits (e.g. are we really going to give up all of our cars? can we?)
 - need to assess the risk involved in our behaviors

Unit 2.3 Summary

Concepts

- definitions of acids and bases
 - · acids produce hydronium when dissolved in aqueous solutions
 - bases produce hydroxide when dissolved in aqueous solutions
- acid-base equilibria and neutralization
 - acid + base → salt + water
 - $[H_3O^+]$ * $[OH^-]$ = 1 x 10⁻¹⁴ (a constant)
- definition of pH
 - pH = $-log[H_3O^+]$
- nitrogen cycle
- Questions to organize your thoughts:
 - Which substances are acidic? Which are basic? How do we find out (measure)?
 - How do acid-base equilibria work?
 - What are the sources of "extra" acidity in rain?
 - What are the biological and/or environmental consequences of acid rain?
 - How does the nitrogen cycle work, how do people impact the amounts of nitrogencontaining compounds, and what are the consequences?
 - What are the ways we might reduce sources of acid rain?

Bonding Recap

Covalent bond

- equal sharing of electrons between two atoms
- example: N₂, :N≡N:, :N:::N:

Polar covalent bond

- unequal sharing of electrons between two atoms
- element with the higher electronegativity (EN) holds the electron pair more closely
- example: H₂O
- covalent compound: atoms present in fixed proportions, bonding between atoms is of the (polar) covalent flavor

Ionic bond

- electrostatic interaction between a cation (+) and an anion (-)
- polyatomic ions: two or more ions are covalently bound together; that species carries a positive or negative charge
- ionic compound: ions are present in fixed proportions and arranged in a regular geometric pattern; ions break apart when dissolved

Hydrogen bond

- intermolecular interaction between polar species
- partial positive charge on H; partial negative charge on other atom (N, O, F)

Unit 2.2 Summary

Concepts

- electronegativity → polar bonds → polar molecules (sometimes)
- hydrogen bonding: effects on melting and boiling points; effects on solubility
- ions and ionic compounds
 - anions (-)
 - cations (+)
 - · polyatomic ions
- concentration terms
 - ppm = mg solute /L H₂O
 - ppb = μ g solute /L H₂O
 - molarity (M) = mol solute/L solution
- Questions to organize your thoughts:
 - What makes water an unusual compound?
 - What is our water used for?
 - How is our drinking water purified?
 - What are "safe" levels of minerals and/or contaminants?