## Chapter 6: Neutralizing the Threat of Acid Rain

Is normal rain acidic?

Is acid rain worse in some parts of the country?

Is there a way to “neutralize” acid rain?

One way to define an **acid** is as a substance that releases hydrogen ions, $H^+$, in aqueous solution.

Since the hydrogen ion has no electron, and only one proton (hence the positive charge), the hydrogen ion sometimes is referred to as a **proton**.

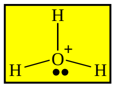
Consider hydrogen chloride gas, dissolved in water:

$$HCl(g) \xrightarrow{H_2O} \underset{\text{(a proton)}}{H^+(aq)} + Cl^-(aq)$$

H⁺ ions are much too reactive to exist alone, so they attach to something else, such as to water molecules.

When dissolved in water, each HCl donates a proton ($H^+$) to an $H_2O$ molecule, forming $H_3O^+$, the hydronium ion.

The $Cl^-$ (chloride) ion remains unchanged.



Hydronium ion. Often we simply write $H^+$, but understand it to mean $H_3O^+$ when in aq. solutions.

The overall reaction is:

$$HCl(g) + H_2O(l) \longrightarrow \underset{\text{hydronium ion}}{H_3O^+(aq)} + Cl^-(aq)$$

The flip side of the story is the chemical opposite of acids: bases.

A **base** is any compound that produces hydroxide ions ($OH^-$) in aqueous solution.

Characteristic properties of bases:

- Bitter taste (not recommended)
- Slippery feel when dissolved in water
- Turn red litmus paper blue

$$\underset{\text{Sodium hydroxide}}{NaOH(s)} \xrightarrow{H_2O} \underset{\text{Sodium ion}}{Na^+(aq)} + \underset{\text{Hydroxide ion}}{OH^-(aq)}$$

Calcium hydroxide produces 2 equivalents of $OH^-$:

$$Ca(OH)_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2OH^-(aq)$$

What about ammonia ($NH_3$)? It is a base, but has no $OH^-$ group

$$NH_3(aq) + H_2O(l) \longrightarrow NH_4OH(aq) \text{ ammonium hydroxide}$$

$$NH_4OH(aq) \xrightarrow{H_2O} NH_4^+(aq) + OH^-(aq)$$

When acids and bases react with each other, we call this a **neutralization reaction**.

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

In **neutralization** reactions, hydrogen ions from an acid combine with the hydroxide ions from a base to form molecules of water.

The other product is a salt (an ionic compound).

Consider the reaction of hydrobromic acid with barium hydroxide.

This reaction may be represented with a molecular, ionic, or net ionic equation:

Molecular:

$2\,HBr(aq) + Ba(OH)_2(aq) \longrightarrow BaBr_2(aq) + 2\,H_2O(l)$

Ionic:

$2\,H^+(aq) + 2\,Br^-(aq) + Ba^{2+}(aq) + 2\,OH^-(aq) \longrightarrow Ba^{2+}(aq) + 2\,Br^-(aq) + 2\,H_2O(l)$

Net Ionic:

$2\,H^+(aq) + 2\,OH^-(aq) \longrightarrow 2\,H_2O(l)$

or by dividing both sides of the equation by 2 to simplify it:

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

---

$2\,HBr(aq) + Ba(OH)_2(aq) \longrightarrow BaBr_2(aq) + 2\,H_2O(l)$

How did we go from Ionic to Net Ionic?

Ionic:

$2\,H^+(aq) + \boxed{2\,Br^-(aq)} + \boxed{Ba^{2+}(aq)} + 2\,OH^-(aq) \longrightarrow \boxed{Ba^{2+}(aq)} + \boxed{2\,Br^-(aq)}$

$+2H_2O(l)$

Remove the species that appear unchanged on both sides of the reaction – these are called **spectator ions**.

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$2\,HBr(aq) + Ba(OH)_2(aq) \longrightarrow BaBr_2(aq) + 2\,H_2O(l)$

How did we go from Ionic to Net Ionic?

Ionic:

$2\,H^+(aq) + \boxed{2\,Br^-(aq)} + \boxed{Ba^{2+}(aq)} + 2\,OH^-(aq) \longrightarrow \boxed{Ba^{2+}(aq)} + \boxed{2\,Br^-(aq)} + 2\,H_2O(l)$

spectator ions

Net Ionic:

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

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One useful relationship is the expression:

$$K_w = [H^+][OH^-] = 1 \times 10^{-14} \quad (\text{at } 25\ ^oC)$$

where $K_w$ is the ion-product constant for water. Knowing the hydroxide ion concentration, we can calculate the $[H^+]$ and vice versa.

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The **pH** of a solution is a measure of the concentration of the $H^+$ ions present in that solution.

The mathematical expression for pH is a log-based scale and is represented as:

$$pH = -\log[H^+]$$

So for a solution with a $[H^+] = 1.0 \times 10^{-3}$ M,

$$pH = -\log(1.0 \times 10^{-3}) = -(-3.0) = 3.0$$

Since pH is a log scale based on 10, a pH change of 1 unit represents a power of 10 change in $[H^+]$.

That is, a solution with a pH of 2 has a $[H^+]$ ten times that of a solution with a pH of 3.

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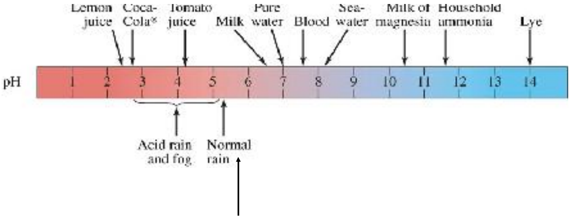
To measure the pH in basic solutions, we make use of the expression to calculate either $[H^+]$ or $[OH^-]$.

$$K_w = [H^+][OH^-] = 1 \times 10^{-14} \quad (\text{at } 25\ ^oC)$$

The three possible aqueous solution situations are:

| | |
|---|---|
| $[H^+] = [OH^-]$ | a neutral solution ($pH = 7$) |
| $[H^+] > [OH^-]$ | an acidic solution ($pH < 7$) |
| $[H^+] < [OH^-]$ | a basic solution ($pH > 7$) |

Common substances and their pH values



Note that “normal” rain is slightly acidic.

Over the past 200 years, the amount of carbon dioxide in the atmosphere has increased, so more carbon dioxide is dissolving in the ocean and forming carbonic acid.

$CO_2(g) + H_2O(l) = H_2CO_3(aq)$

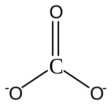
$H_2CO_3(aq) = H^+(aq) + HCO^-_3(aq)$ Partial dissociation

$HCO^-_3(aq) = H^+(aq) + HCO^{2-}_3(aq)$

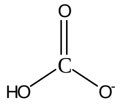
**Ocean acidification –** the lowering of ocean pH due to increased atmospheric carbon dioxide.

If rainwater is naturally acidic, why is ocean water basic?

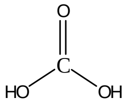
Three chemical species responsible for maintaining ocean pH, they interact with each other:



carbonate ion
$CO_3^{2-}$ *(aq)*



bicarbonate ion
$HCO_3^-$ *(aq)*



carbonic acid
$H_2CO_3$ *(aq)*

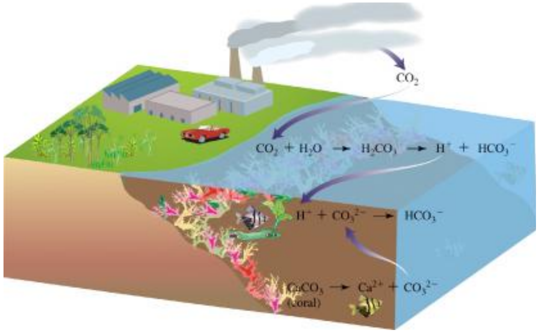
How does this affect availability of $CO_3^{2-}$ for incorporation into marine animal shells and skeletons? The $H^+$ produced from the dissociation of carbonic acid reacts with carbonate ion in seawater to form the bicarbonate ion:

$$H^+(aq) + CO_3^{2-}(aq) \rightarrow HCO_3^-(aq)$$

This reduces the concentration of carbonate ion in seawater, so the calcium carbonate in the shells of sea creatures begins to dissolve to maintain the concentration of carbonate ions in seawater:

$$CaCO_3(s) \rightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$$

**Chemistry of Carbon Dioxide in the Ocean**



Since 1800’s the pH of the oceans has dropped by 0.1;
i.e. 26% increase of $[H^+]$. Extra acidity reacts with carbonate ions in the ocean water. To replenish it back shells, corals and other sources of $CaCO_3$ must dissolve.

In 200 years the pH of oceans have changed to levels not seen in 400 million years.

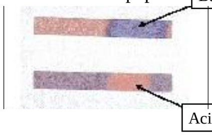
Poses a threat to marine life forms.

Reduces the formation of corals and coral reefs, decreasing the protections against storms for coastal areas.

Ocean temperatures are on the rise, which changes pH as well.

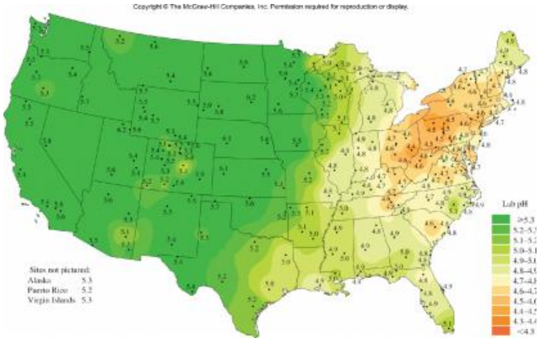
Measuring pH with a pH meter

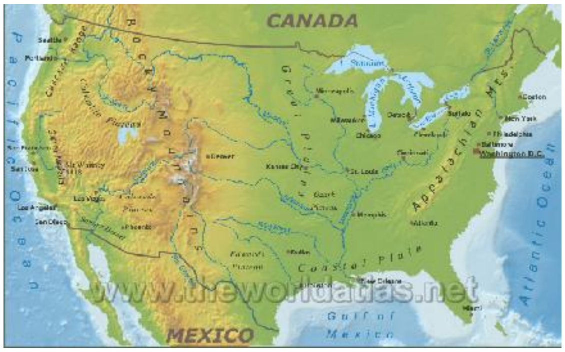
Or with litmus paper



Base applied to red litmus

Acid applied to blue litmus





Why is rain *naturally* acidic?

Carbon dioxide in the atmosphere dissolves to a slight extent in water and reacts with it to produce a slightly acidic solution of carbonic acid:

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq) \text{ carbonic acid}$$

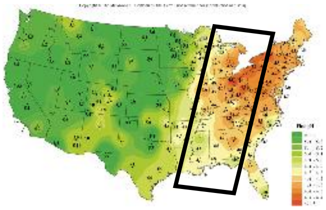
$$H_2CO_3(aq) \longrightarrow H^+(aq) + HCO_3^-(aq)$$

The carbonic acid dissociates slightly leading to rain with a pH around 5.3 (5 - 6, normal).

Acid rain can have pH levels lower than 4.3 – where is the extra acidity coming from?

The most acidic rain falls in the eastern third of the United States, with the region of lowest pH being roughly the states along the Ohio River valley.

The extra acidity must be originating somewhere in this heavily industrialized part of the country.



Analysis of rain for specific compounds confirms that the chief culprits are the oxides of sulfur and nitrogen:

sulfur dioxide ($SO_2$), sulfur trioxide ($SO_3$), nitrogen monoxide (NO), and nitrogen dioxide ($NO_2$).

These compounds are collectively designated $SO_x$ and $NO_x$ and are often referred to as “Sox and Nox.”

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Oxides of sulfur and nitrogen are **acid anhydrides**, literally “acids without water.”

$SO_x$ react with water to form acids:

$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$ sulfurous acid

$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$ sulfuric acid

*And then*: $H_2SO_4(aq) \longrightarrow 2\,H^+(aq) + SO_4^{2-}(aq)$

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What about the $NO_x$?

$4\,NO_2(g) + 2\,H_2O(l) + O_2(g) \longrightarrow 4\,HNO_3(aq)$
nitric acid

Like sulfuric acid, nitric acid also dissociates to release the $H^+$ ion:

$HNO_3(aq) \longrightarrow \boxed{H^+(aq)} + NO_3^-(aq)$

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**Sulfur dioxide** emissions are highest in regions with many coal-fired electric power plants, steel mills, and other heavy industries that rely on coal.

Allegheny County, in western Pennsylvania, is just such an area, and in 1990 it led the United States in atmospheric $SO_2$ concentration.

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How does the sulfur get into the atmosphere?

The burning of coal. Coal contains 1–3% sulfur and coal burning power plants usually burn about 1 million metric tons of coal a year!

Burning of sulfur with oxygen produces sulfur dioxide gas, which is poisonous.

$S(s) + O_2(g) \longrightarrow SO_2(g)$

$SO_2$ can react with oxygen molecules to form sulfur trioxide, which acts in the formation of aerosols.

$2\,SO_2(g) + O_2(g) \xrightarrow{\text{Ash/particles – cat.}} 2\,SO_3(g)$

$SO_2(g) + \cdot OH(g) \rightarrow SO_3$

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<u>Metal Manufacturing Processes:</u>

Metals ores exist as sulfides; NiS and CuS.

Extraction of metal involve heating the MS with air.

The process generates extremely large quantities of $SO_2$ into air.

The highest **$NO_x$** emissions are generally found in states with large urban areas, high population density, and *heavy automobile* traffic.

The highest levels of atmospheric $NO_2$ are measured over Los Angeles County, the car capital of the country.

Nitrogen dioxide gas in the atmosphere reacts with the hydroxyl radical to form nitric acid.

$$NO_2(g) + \cdot OH(g) \rightarrow HNO_3(l)$$

$$\uparrow$$

$$O_3 + H_2O + h\nu \rightarrow OH^{o}$$

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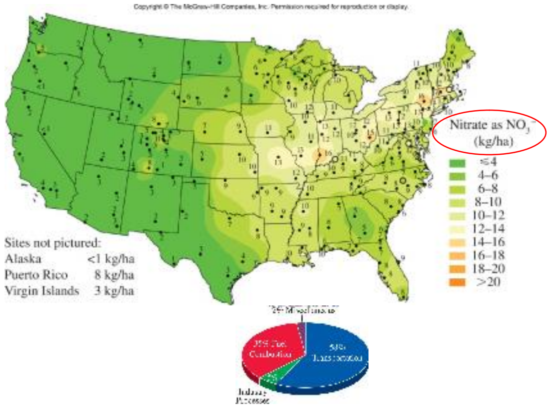

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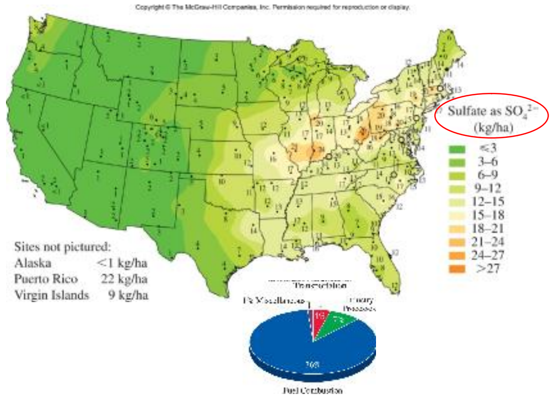


Other forms of acid deposition.

Snow and fog.

Mountain tops are particularly susceptible to wet deposition (from clouds); small droplets concentrate more acid than rain drops..

Dry forms of acid, aerosols of $NH_4NO_3$, $(NH_4)_2SO_4$ – summer.

Nox and Gasoline Combustion.

1982 recorded pH of acid rain –

@Rose Bowl - 2.5 (~ vinegar)
@Corona Del Mar pH = 1.5.

Reason – not $CO_2$ or Sox but Nox generated in automobile gas engines.

$N_2$ comes from air (80%).

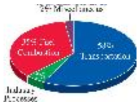
Direct Source of Nitrogen Oxides

$$N_2 + O_2 + \text{high temp} \rightarrow 2\ NO$$

(nitrogen oxide)

**High temperatures in auto engine or coal-fired power plant**

NO is very reactive:



$$2\ NO + O_2 \rightarrow 2\ NO_2$$

$$NO + O_3 \rightarrow 2\ NO_2$$

(nitrogen dioxide)

## Role of Volatile Organic Compounds (VOCs)

VOCs = Compounds that easily evaporate under normal temperatures.
Sources: incompletely burnt gasoline, leaks and spills from manufacturing plants of organic materials, forests.

$$VOC + {}^{\bullet}OH \rightarrow A$$
$$A + O_2 \rightarrow A'$$
$$A' + NO \rightarrow A'' + NO_2$$

Hydroxyl radical, ${}^{\bullet}OH$, exist in air in very small amounts.

$$NO_2(g) + \cdot OH(g) \rightarrow HNO_3(l)$$

## Agricultural Practices:

Food production involves the generation of Nox .

Plant growth assimilates the elements C, H, S, P and N (in usable forms $NH_4^+$, $NH_3$ and $NO_3^-$).

Plants need nitrogen in chemical forms that is utilized more easily, the ammonium ion, ammonia, or the nitrate ion, in order to grow.

N is scarce in nature.

Natural N-fixing (bacteria living in/near roots of plants or in soil) form atmosphere is insufficient.

N is supplied for plant growth, at industrial scale manufacturing enterprises as fertilizer as $NH_4^+$, $NH_3$ and $NO_3^-$.

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Bacterial action 'fixes $N_2$':

$$N_2 \rightarrow NH_3 \rightarrow NH_4^+$$

Nitrification;

$$NH_3 \rightarrow NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$$

De-nitrification;

$$NO_3^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

## Simplified Nitrogen Cycle

A set if chemical pathways that moves N through the biosphere.

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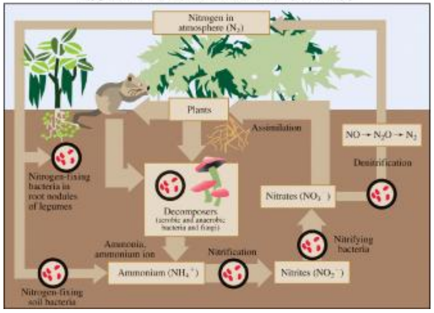


Haber-Bosch process for large scale fertilizer production:

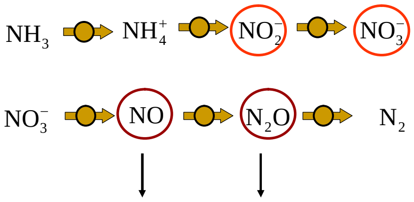
$$N_2(g) + H_2(g) \rightarrow 2\ NH_3(g)$$

The ammonia produced is converted to ammonium nitrate, or ammonium phosphate (fertilizers).

Haber processes makes the modern agricultural practices possible.

(N and P of NPK fertilizers)

Enters the environment – leaching or release as a gas.



$NH_3 \rightarrow NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$

$NO_3^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

Green house gases, acid rain precursors.

Sox and Nox enters the environment naturally and anthropogenic.

S: antropogenic ~ 2 × natural,
N: anthropogenic ~ 4 × natural.

Natural:

Volcanoes ⇒ S and Sox
Marine organisms – $(CH_3)_2S$; $(CH3)_2S + OH^o \Rightarrow SO_2$
Lightening ⇒ NO
Soil bacteria ⇒ NO

Emissions of $NO_x$ and $SO_2$ in the U.S.

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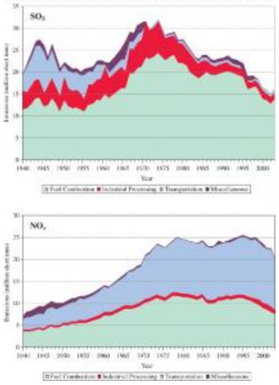

Effects of acid rain: rusting metal

Iron metal dissolves when exposed to hydrogen ions:

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

Now the aqueous $Fe^{2+}$ ions react with oxygen to form rust ($Fe_2O_3$):

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

Billions of dollars are spent annually to protect bridges, cars, buildings, and ships from the reactions above.

Effects of acid rain: damage to marble

1944 At present

These statues are made of marble, a form of limestone composed mainly of calcium carbonate, $CaCO_3$. Limestone and marble slowly dissolve in the presence of $H^+$ ions:

$$CaCO_3(s) + 2\ H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$$

## Haze, Acid Deposition and Human Health.

Coal burning → smoke and particulate matter (Haze)
Soil dust, burning wood → (Haze)
Tiny droplets (aerosol) → (Haze)

Nox and $SO_2$ are precursors to haze.

$SO_2$ is hygroscopic. $SO_2$ oxidizes to $SO_3$;
water + $SO_3$ → $H_2SO_4$ droplets (aerosol). – (Haze)

$H_2SO_4$ droplets (aerosol), reacts with bases like ammonia.

water + $SO_3$ → $H_2SO_4$ (sunlight catalyst)

Breathing acidic water droplets:

affects lungs (asthma, emphysems, cardiovascualar disease.

mortal for individuals with bronchitis, pneumonia.

Cheap electricity is very expensive from public health point of view.

Solubility of toxic metal ions in minerals increases posing a public health threat.

## Acid rain damages lakes and streams

Healthy lake:
pH ~6.5,
pH< 6.0 aquatic life affected.

pH<5.0 only hardy species survive.
pH~4 – dead ecosystem.

Soils may neutralize acid rain.
Lakes can neutralize acidity to a point – acid neutralizing capacity is limited (limestone)

$$CaCO_3(s) + 2\,H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$$

## Effects of acid rain: damage to lakes and streams