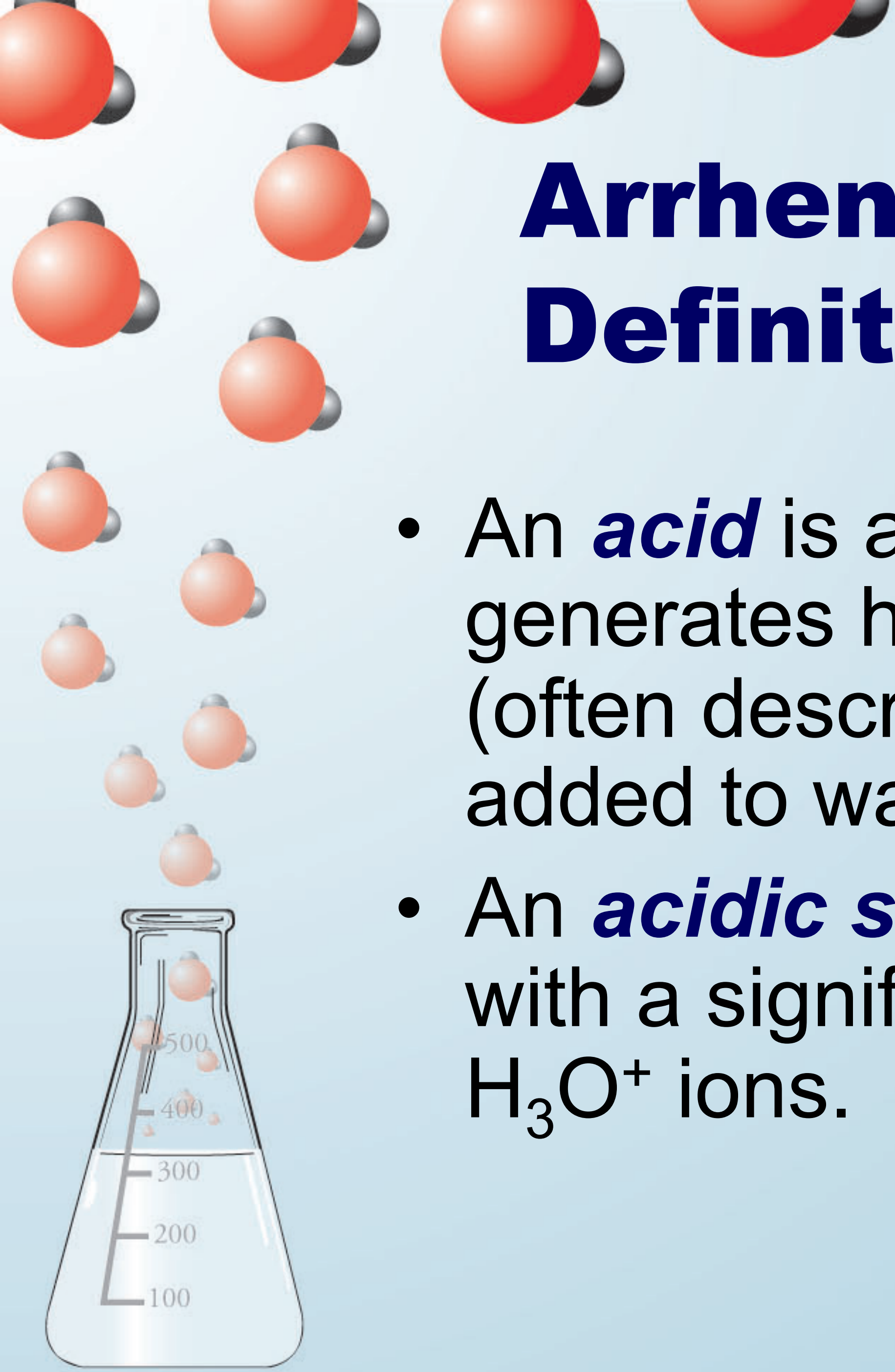
Acids, Bases, pH, Acid Rain, and Ocean Acidification

http://preparatorychemistry.com/Bishop_Book_atoms_6.pdf

http://preparatorychemistry.com/Bishop_Book_atoms_8.pdf

http://preparatorychemistry.com/Bishop_Book_atoms_13.pdf

Arrhenius Acid Definition



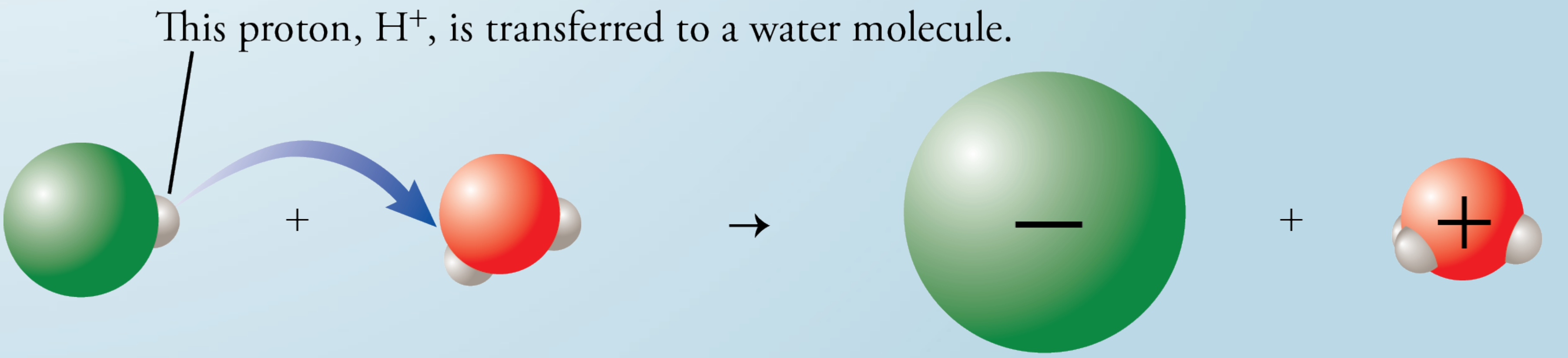
- An ***acid*** is a substance that generates hydronium ions, H_3O^+ (often described as H^+), when added to water.
- An ***acidic solution*** is a solution with a significant concentration of H_3O^+ ions.

Characteristics of Acids

- Acids have a sour taste.
- Acids turn litmus from blue to red.
- Acids react with bases.

Strong Acid and Water

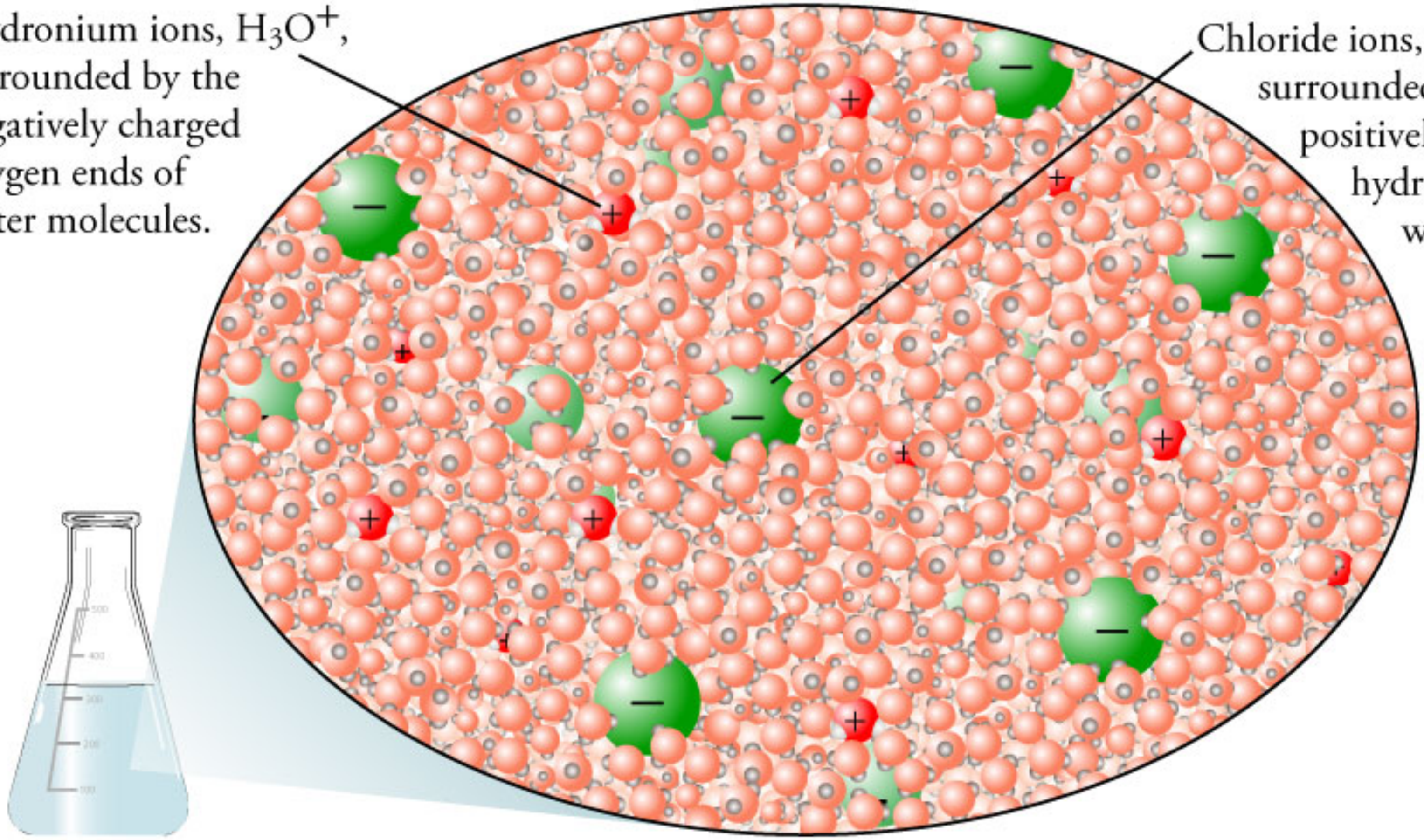
When HCl dissolves in water, hydronium ions, H_3O^+, and chloride ions, Cl^-, ions form.



This proton, H^+, is transferred to a water molecule.

$$HCl(g) + H_2O(l) \rightarrow Cl^-(aq) + H_3O^+(aq)$$

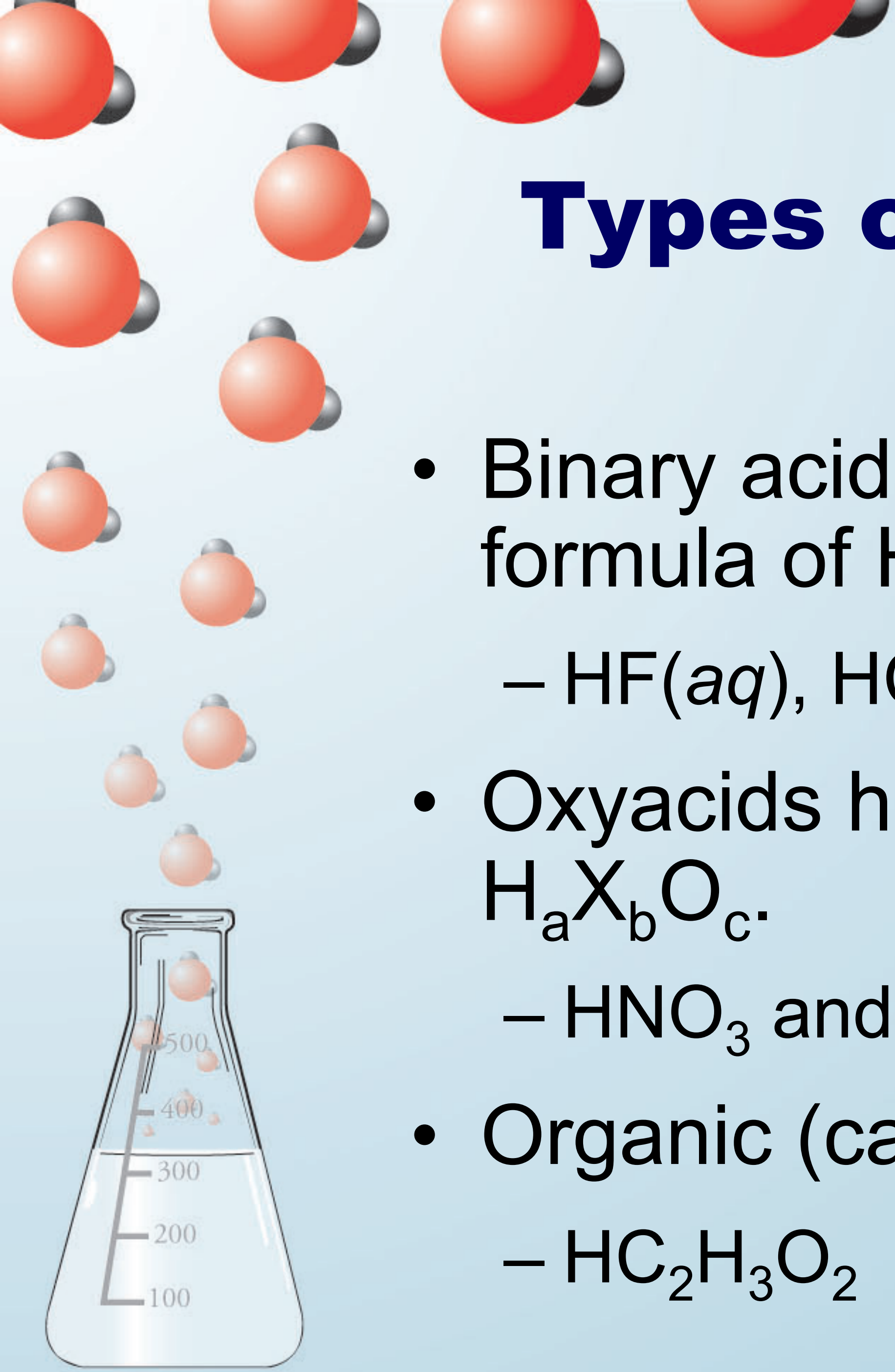
Solution of a Strong Acid



Hydronium ions, H_3O^+, surrounded by the negatively charged oxygen ends of water molecules.

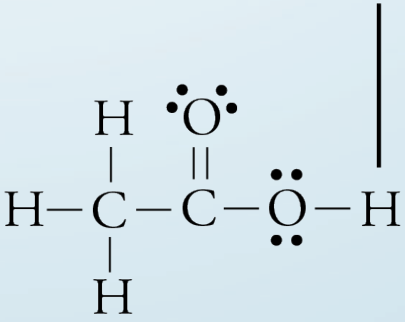
Chloride ions, Cl^-, surrounded by the positively charged hydrogen ends of water molecules.

Types of Acids



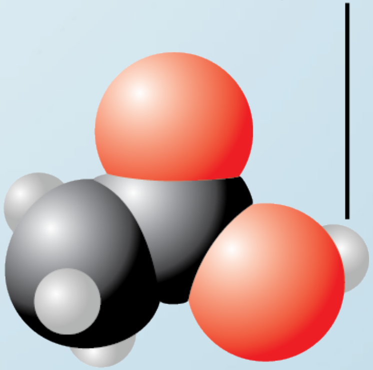
- Binary acids have the general formula of HX(aq)
  - HF(*aq*), HCl(*aq*), HBr(*aq*), and HI(*aq*)
- Oxyacids have the general formula $H_aX_bO_c$.
  - HNO_3 and H_2SO_4
- Organic (carbon-based) acids
  - $HC_2H_3O_2$

Acetic Acid

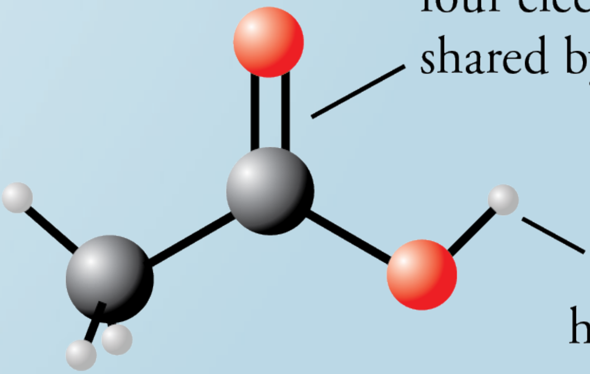


$$\mathrm{H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle \ddot{O}}{\|}}{C}-\underset{\cdot\cdot}{\ddot{O}}-H}$$

Acidic hydrogen

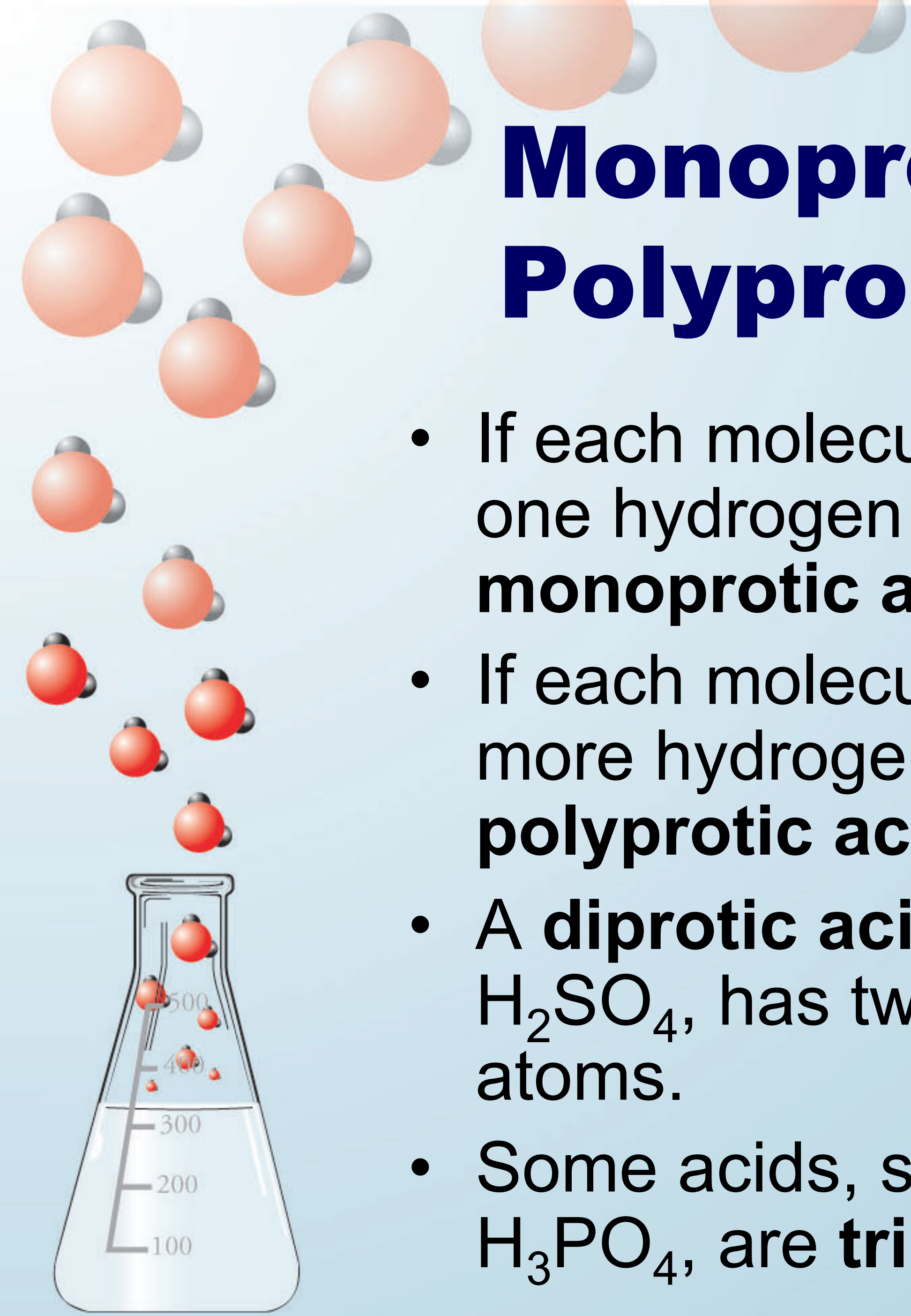


Acidic hydrogen



Double bond, four electrons shared by atoms

Acidic hydrogen



Monoprotic and Polyprotic Acids

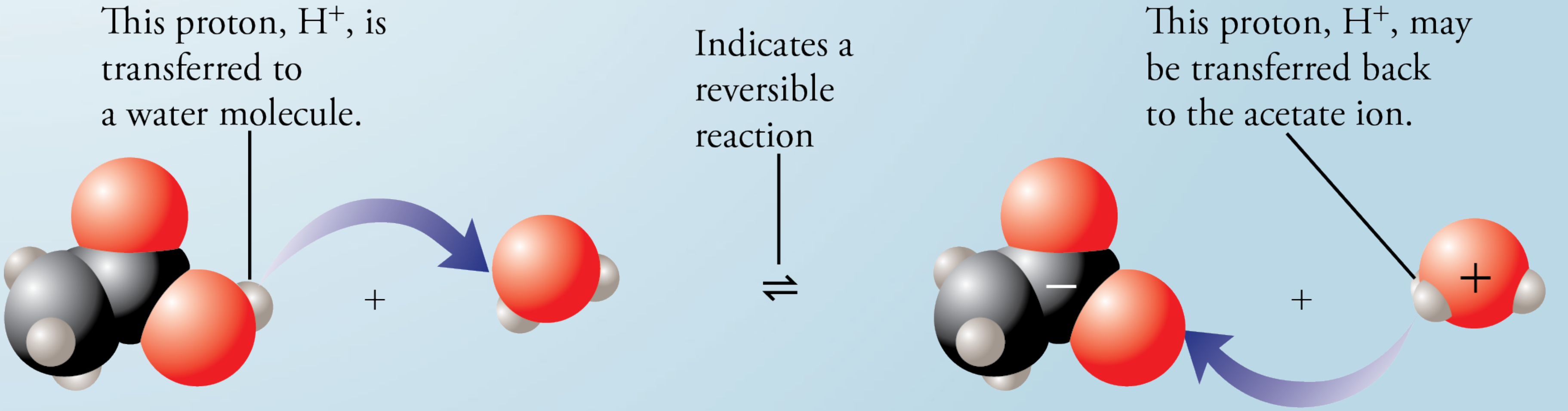
- If each molecule of an acid can donate one hydrogen ion, the acid is called a **monoprotic acid**.
- If each molecule can donate two or more hydrogen ions, the acid is a **polyprotic acid**.
- A **diprotic acid**, such as sulfuric acid, H_2SO_4, has two acidic hydrogen atoms.
- Some acids, such as phosphoric acid, H_3PO_4, are **triprotic acids**.

Strong and Weak Acids

- ***Strong Acid*** = due to a completion reaction with water, generates close to one H_3O^+ for each acid molecule added to water.
- ***Weak Acid*** = due to a reversible reaction with water, generates significantly less than one H_3O^+ for each molecule of acid added to water.

Weak Acid and Water

Acetic acid reacts with water in a reversible reaction, which forms hydronium and acetate ions.


This proton, H^+, is transferred to a water molecule.

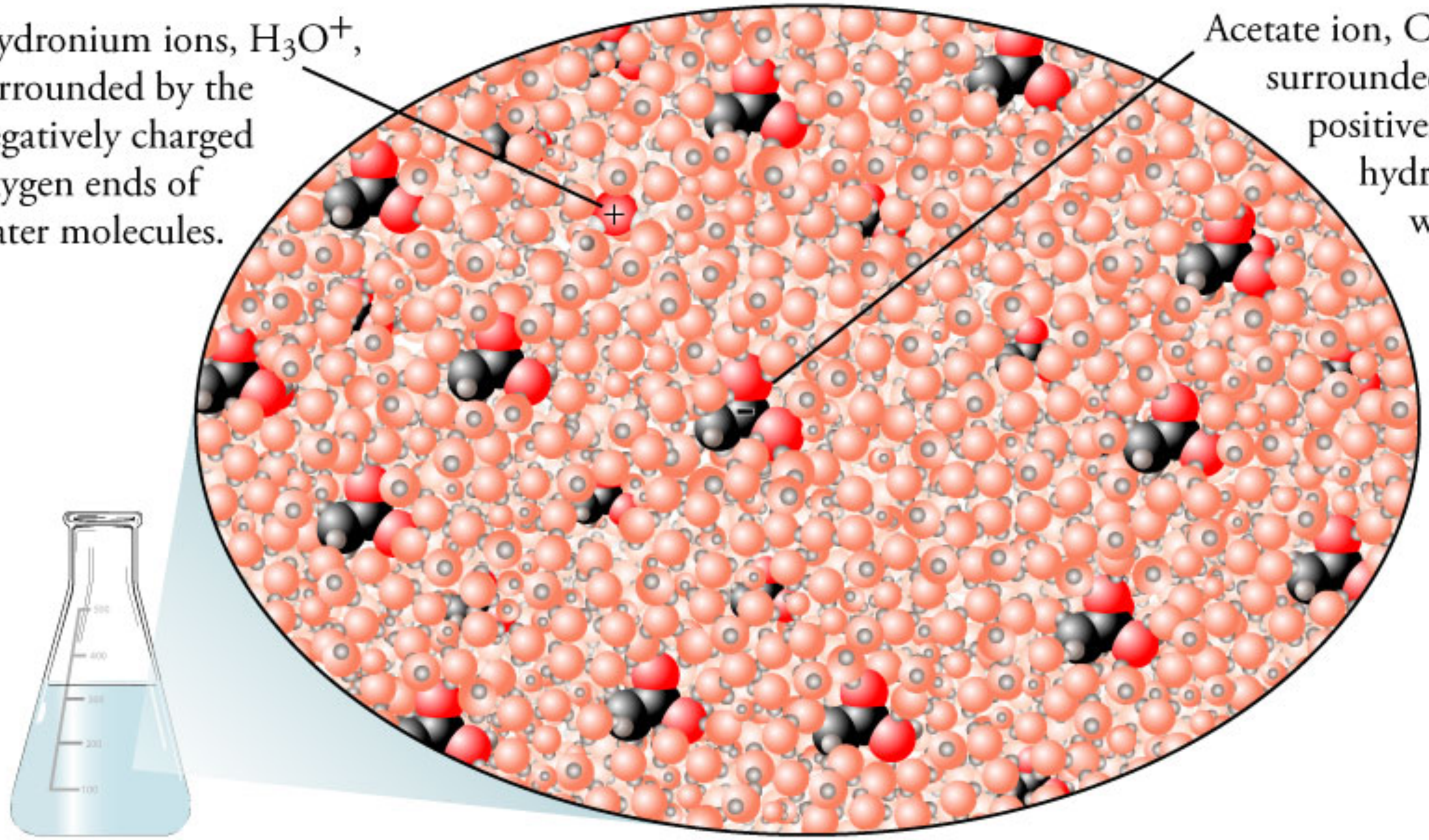
Indicates a reversible reaction

This proton, H^+, may be transferred back to the acetate ion.

$$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons C_2H_3O_2^-(aq) + H_3O^+(aq)$$

Solution of Weak Acid

In a typical acetic acid solution, there areabout 250 times as many uncharged acetic acid molecules, $HC_2H_3O_2$, as acetate ions, $C_2H_3O_2^-$.



Hydronium ions, H_3O^+, surrounded by the negatively charged oxygen ends of water molecules.

Acetate ion, $C_2H_3O_2^-$, surrounded by the positively charged hydrogen ends of water molecules.

Strong and Weak Acids

For every 250 molecules of the weak acid acetic acid, $HC_2H_3O_2$, added to water, there are about

$$HC_2H_3O_2(aq) \quad + \quad H_2O(l) \quad \rightleftharpoons \quad C_2H_3O_2^-(aq) \quad + \quad H_3O^+(aq)$$

249 uncharged acetic acid molecules

One acetate ion

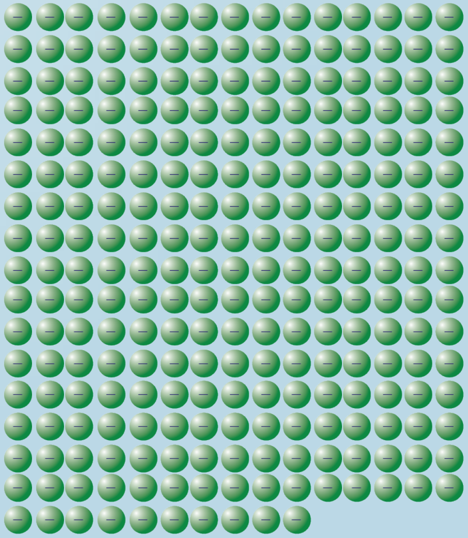
One hydronium ion

For every 250 molecules of the strong acid hydrochloric acid, HCl, added to water, there are about

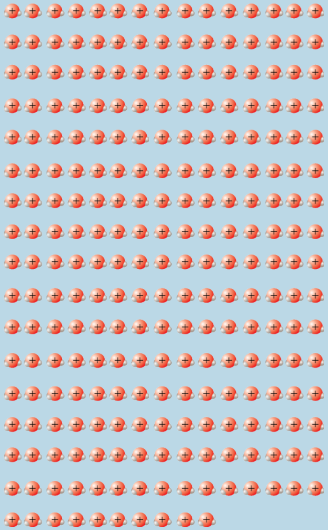
$$HCl(g) \quad + \quad H_2O(l) \quad \rightarrow \quad Cl^-(aq) \quad + \quad H_3O^+(aq)$$

Zero uncharged HCl molecules

250 chloride ions



250 hydronium ions



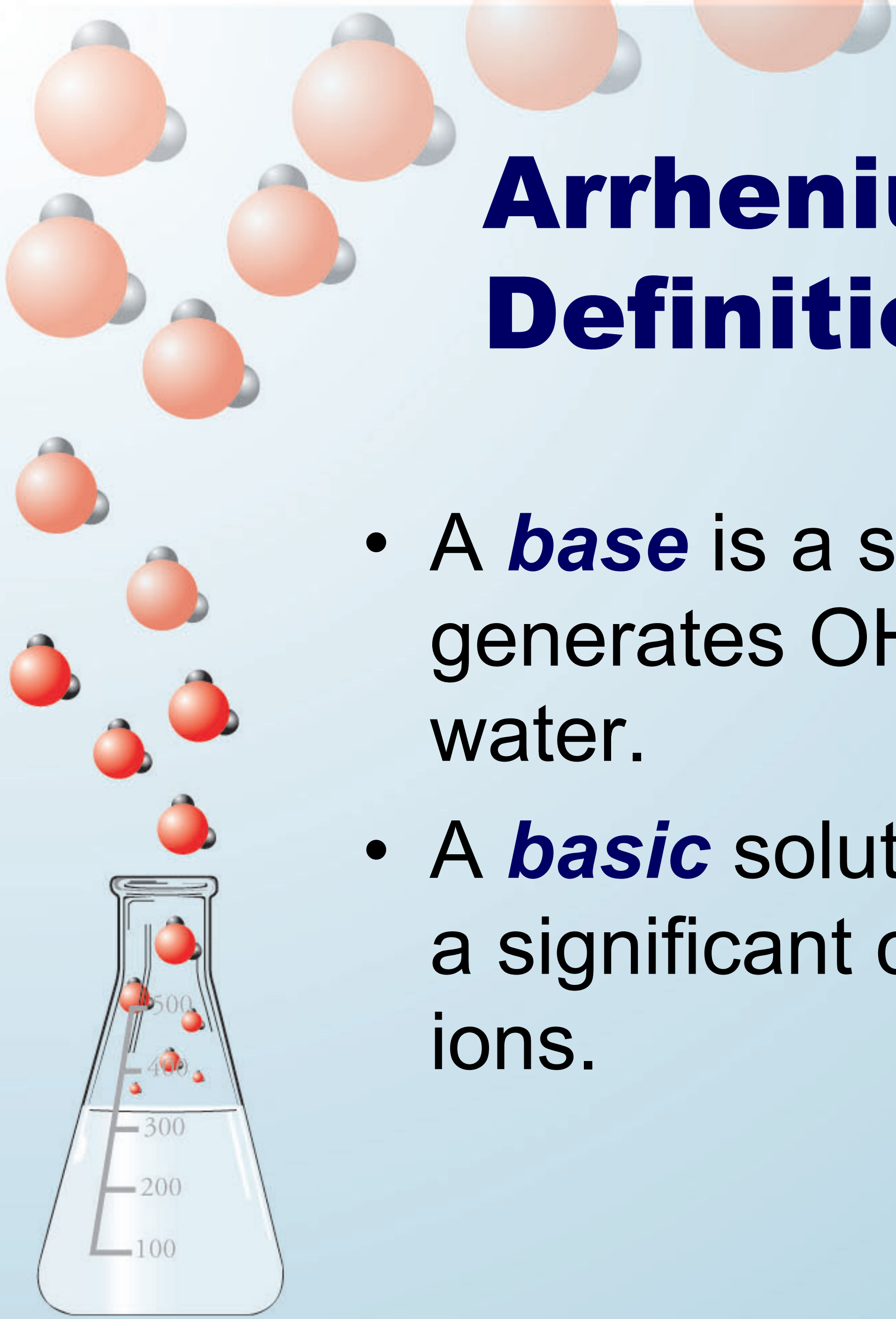
Sulfuric Acid

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$$

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

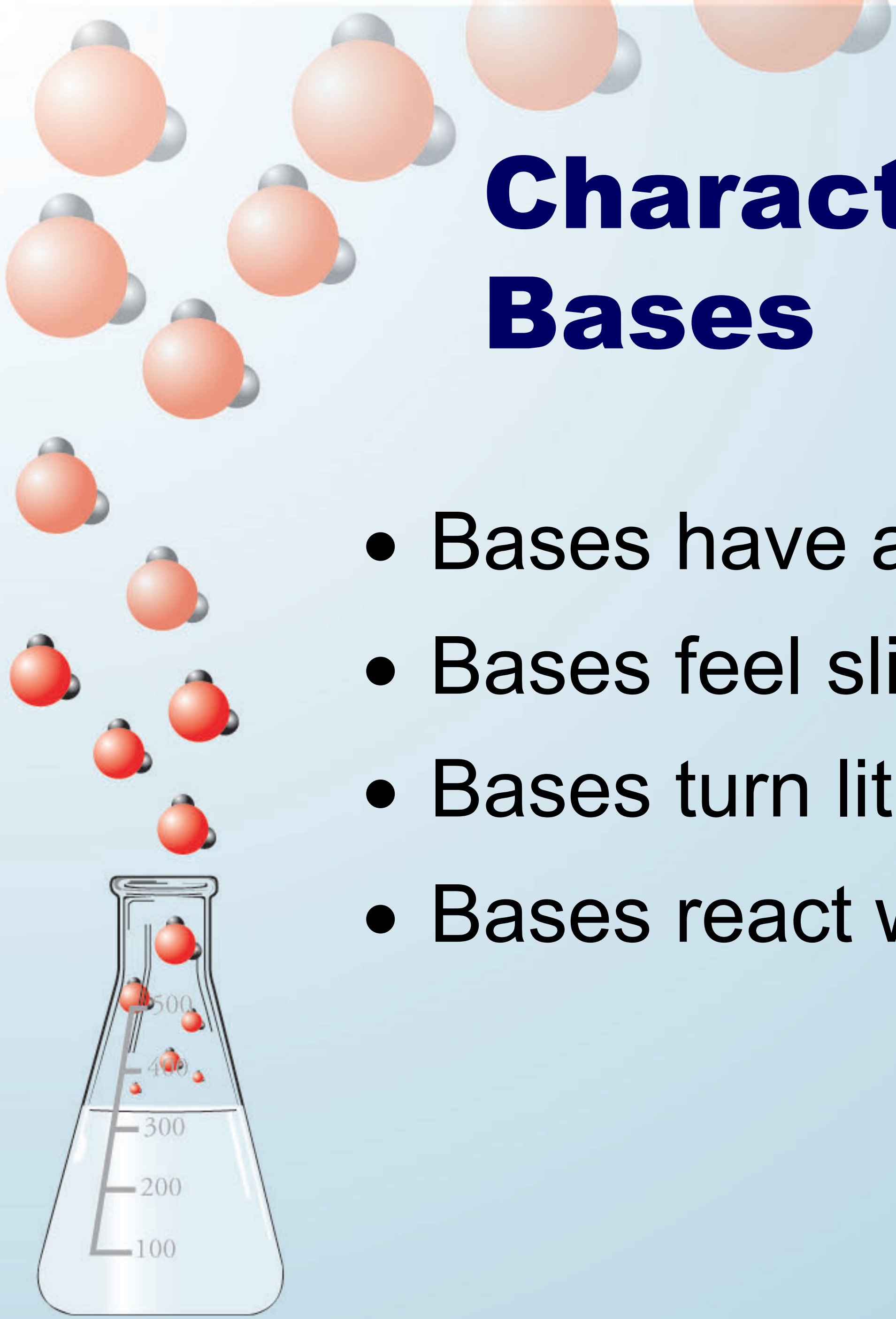
Acid Summary

	Strong	Weak
Binary acid	hydrochloric acid, HCl(aq)	hydrofluoric acid
Oxyacid	nitric acid, HNO_3 sulfuric acid, H_2SO_4	other acids with $H_aX_bO_c$
Organic acid	none	acetic acid, $HC_2H_3O_2$



Arrhenius Base Definitions

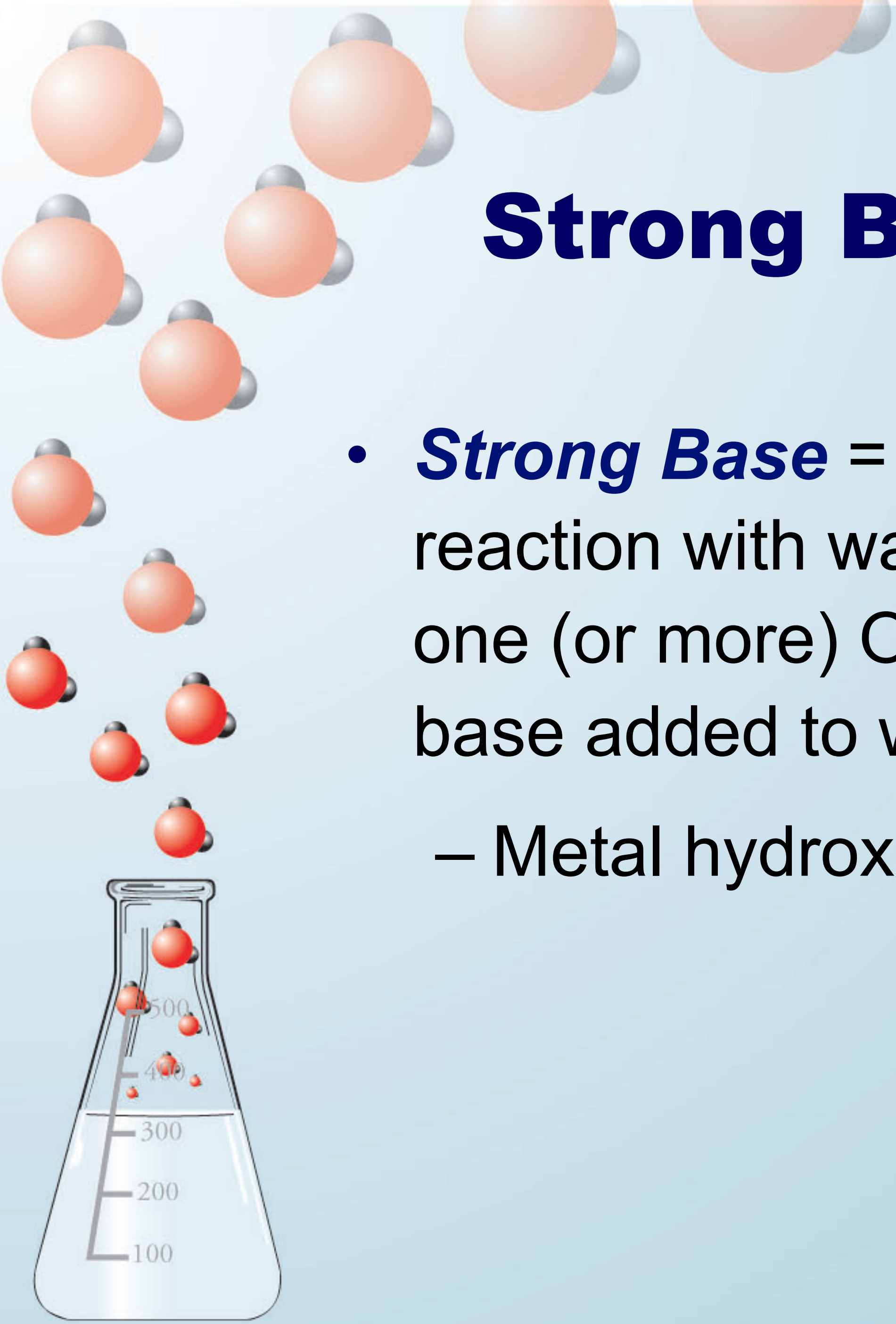
- A ***base*** is a substance that generates OH^- when added to water.
- A ***basic*** solution is a solution with a significant concentration of OH^- ions.



Characteristics of Bases

- Bases have a bitter taste.
- Bases feel slippery on your fingers.
- Bases turn litmus from red to blue.
- Bases react with acids.

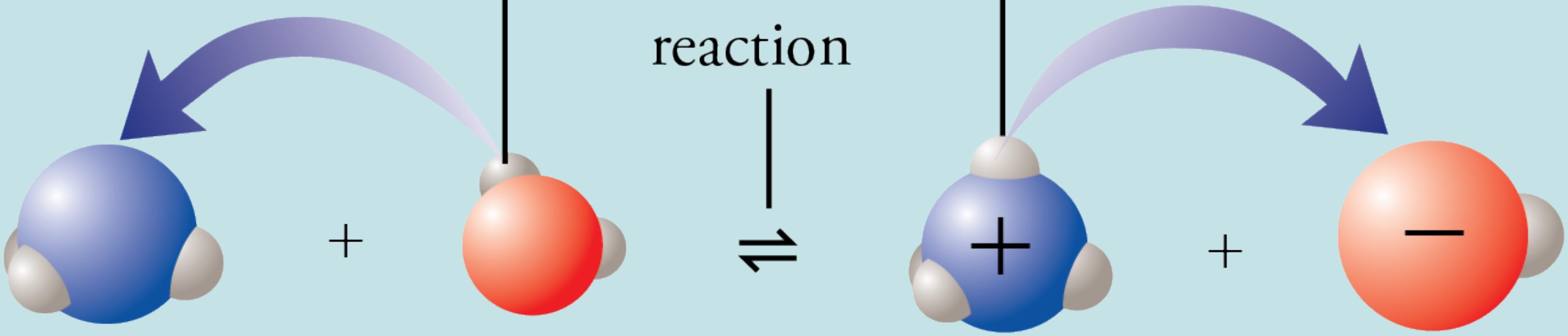
Strong Bases



- ***Strong Base*** = due to a completion reaction with water, generates close to one (or more) OH^- for each formula unit of base added to water.
  - Metal hydroxides are strong bases.

Ammonia and Water

Ammonia reacts with water in a reversible reaction, which forms ammonium and hydroxide ions.



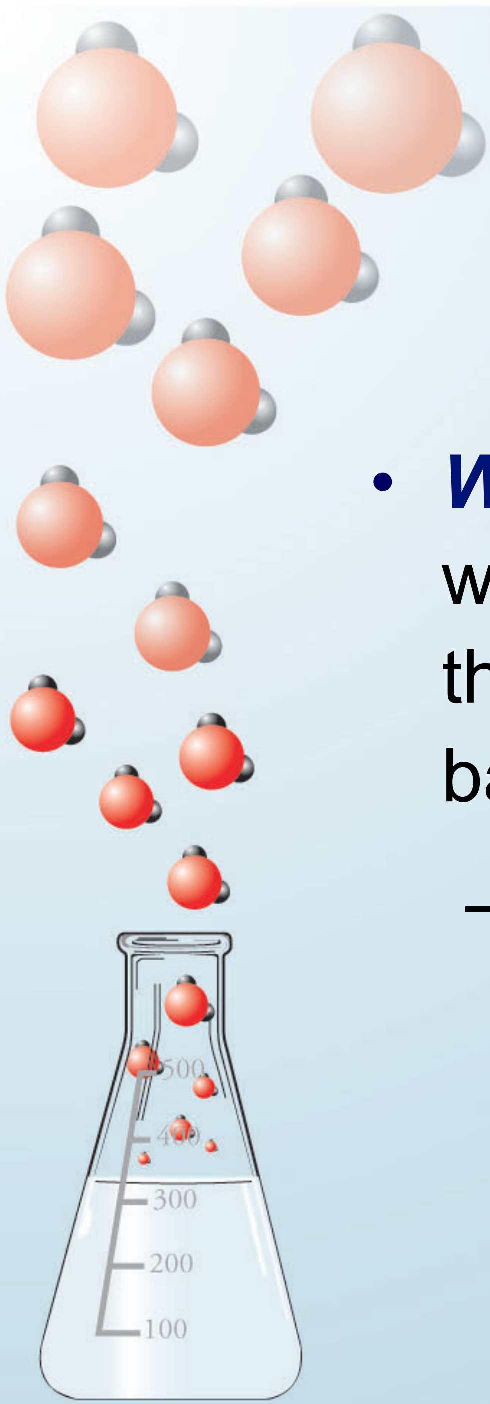
This proton, H^+, is transferred to an ammonia molecule.

Indicates a reversible reaction

This proton, H^+, may be transferred back to the hydroxide ion.

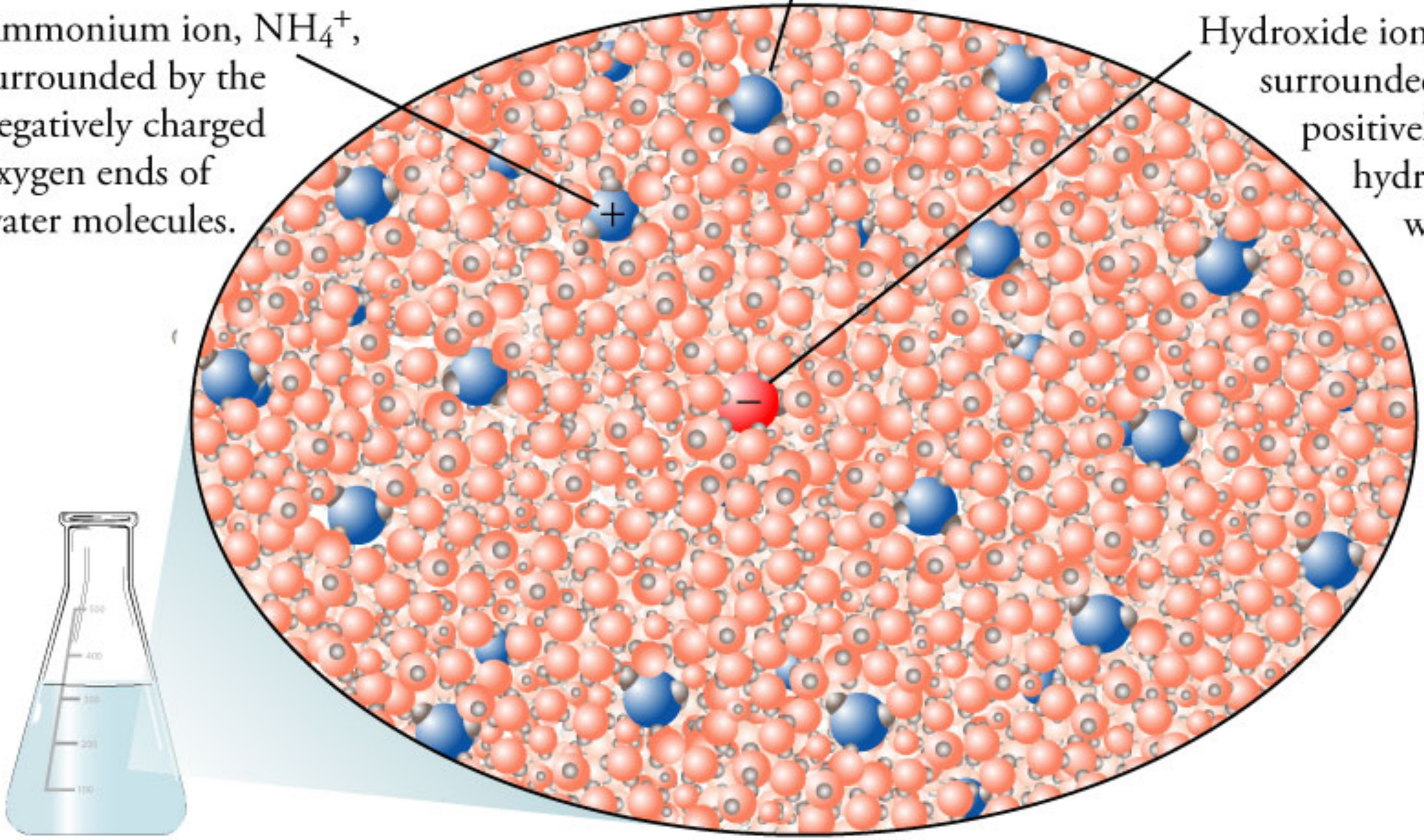
$$NH_3(aq) \quad + \quad H_2O(l) \quad \rightleftharpoons \quad NH_4^+(aq) \quad + \quad OH^-(aq)$$

Weak Base



- ***Weak Base*** = due to a reversible reaction with water, generates significantly less than one OH^- for each formula unit of base added to water.
  - Ammonia and ionic compounds that contain CO_3^{2-} or HCO_3^- are weak bases.

Ammonia Solution



In a typical ammonia solution, there are about 200 times as many uncharged ammonia molecules, NH_3, as ammonium ions NH_4^+.

Ammonium ion, NH_4^+, surrounded by the negatively charged oxygen ends of water molecules.

Hydroxide ion, OH^-, surrounded by the positively charged hydrogen ends of water molecules

Carbonate Bases

$Na_2CO_3(s) \rightarrow 2Na^+(aq) + CO_3^{2-}(aq)$

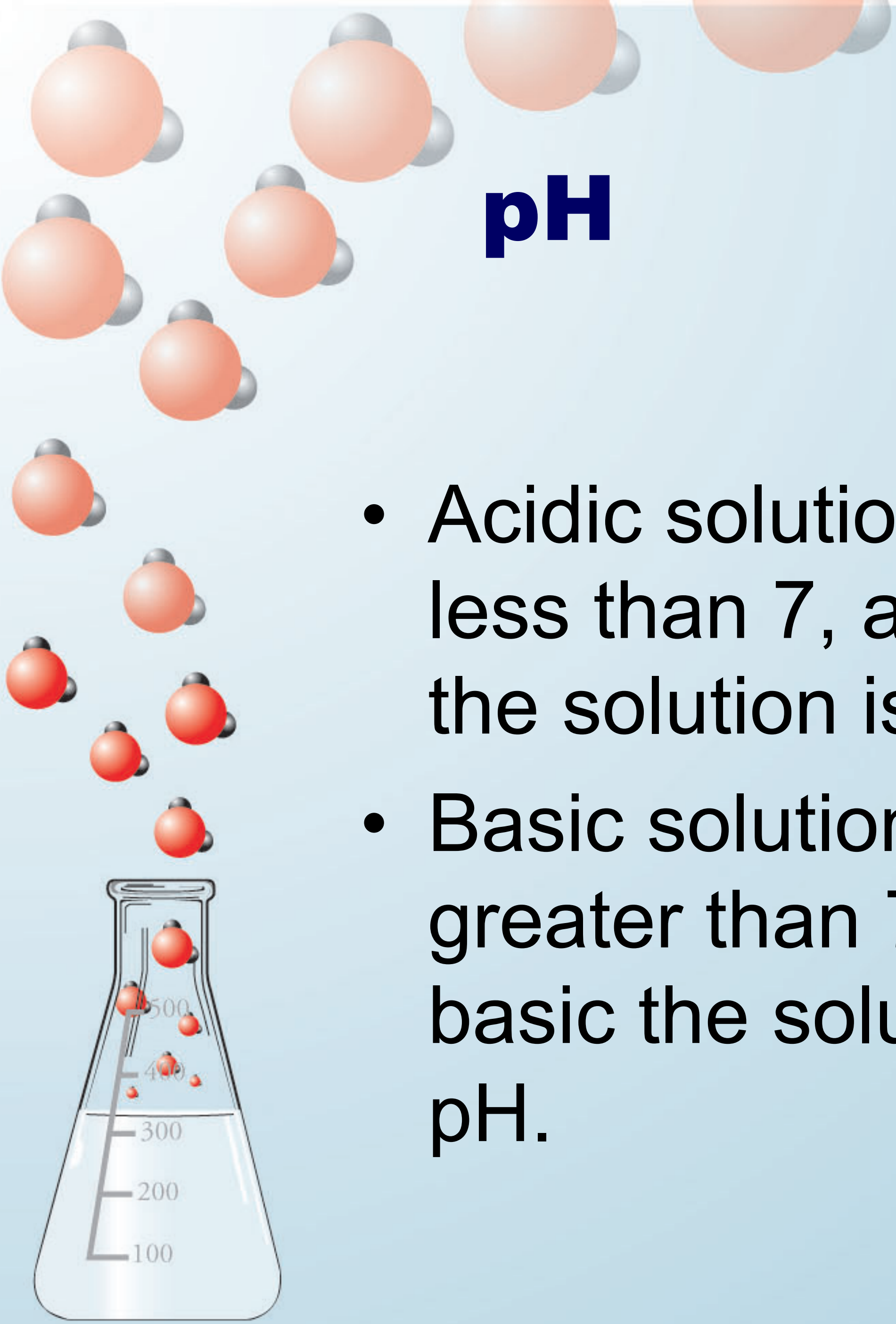
$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

$NaHCO_3(s) \rightarrow Na^+(aq) + HCO_3^-(aq)$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

Arrhenius Bases

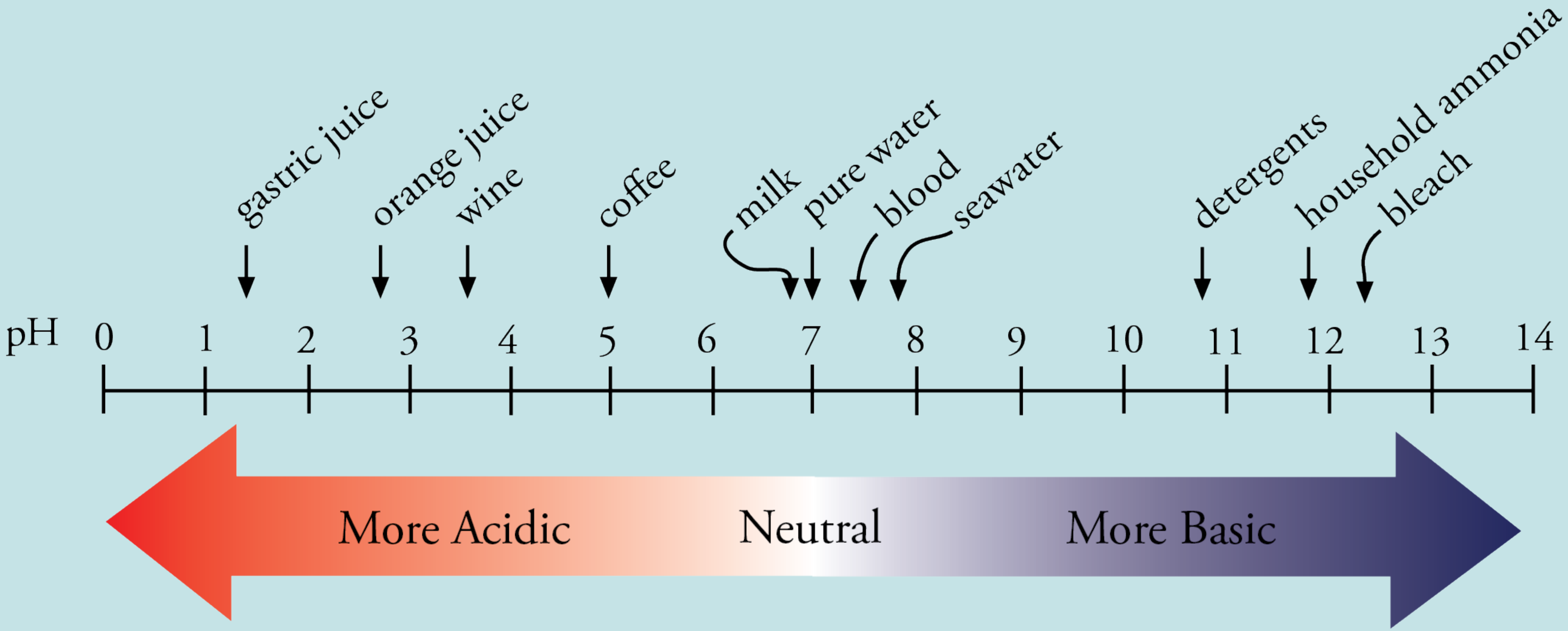
	Strong	**Weak**
Ionic Compounds	Metal hydroxides	Ionic compounds with CO_3^{2-} and HCO_3^-
Certain Uncharged molecules	None	NH_3



pH

- Acidic solutions have pH values less than 7, and the more acidic the solution is, the lower its pH.
- Basic solutions have pH values greater than 7, and the more basic the solution is, the higher its pH.

pH Range


gastric juice
orange juice
wine
coffee
milk
pure water
blood
seawater
detergents
household ammonia
bleach

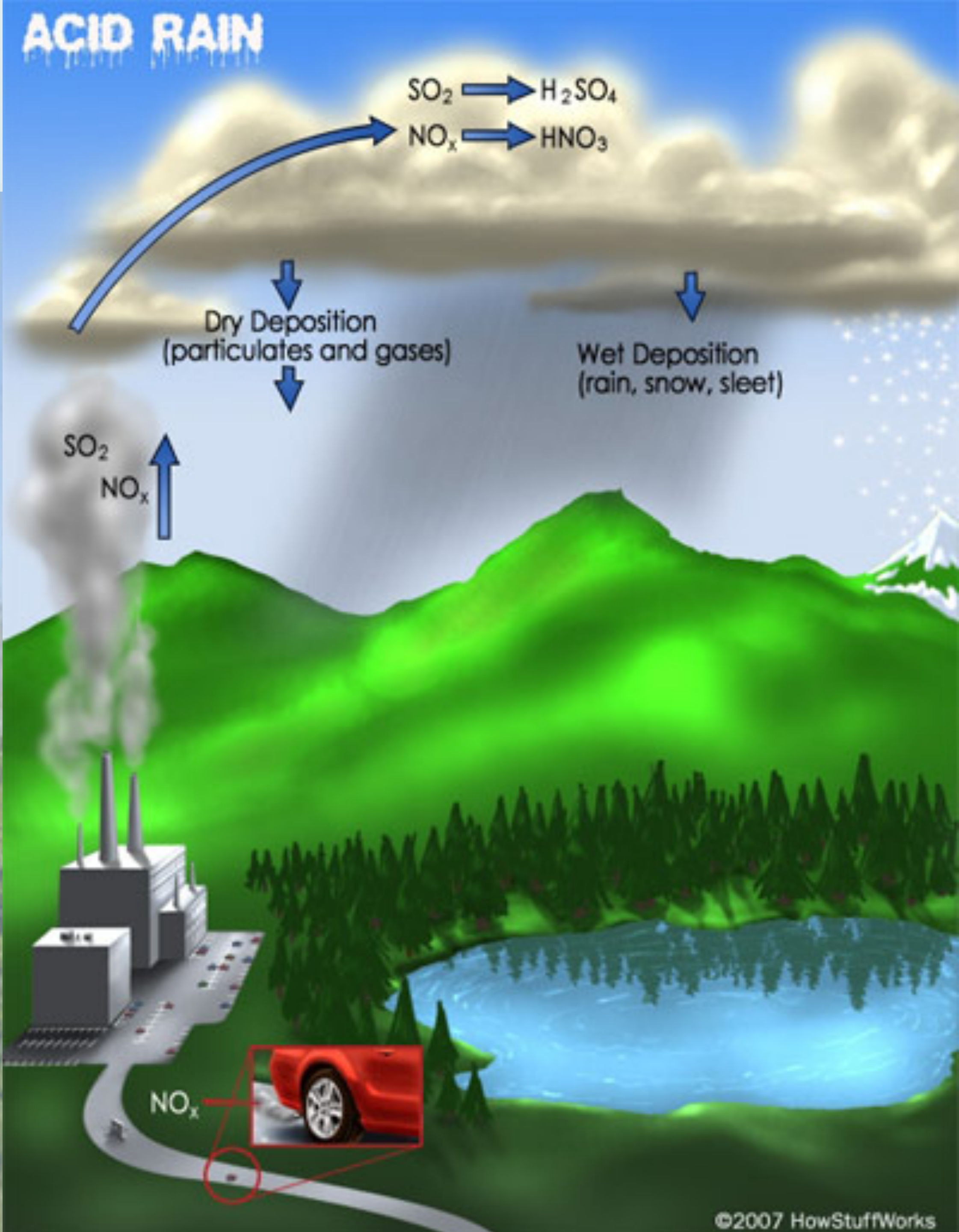
pH 0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

More Acidic
Neutral
More Basic

Acidic solutions have pH values less than 7.

Basic solutions have pH values greater than 7.

Acid Rain


ACID RAIN
$SO_2 \rightarrow H_2SO_4$
$NO_x \rightarrow HNO_3$
Dry Deposition
(particulates and gases)
Wet Deposition
(rain, snow, sleet)
SO_2
NO_x
NO_x
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Acid Deposition

Wet Deposition (acid rain, snow)

- Easy to measure; about half of acid deposition
- First measured in 1852 in England
- No widespread attention until 1961, when Swedish scientists hypothesized that declining fish populations (and, later, forest damage) might be caused by acid rain from coal-burning regions of Europe.
- By 1980, recognized as a major environmental problem in industrialized countries.

Acid Deposition

Dry deposition (acid gases and aerosols)

- Difficult to measure; importance recognized only in 1980s
- Main form of acid deposition near source
- Main cause of damage to foliage?

Droplet deposition (acid fogs)

- Generally less important than wet and dry deposition, except in certain locations
- Highest measured acidities, but total dose small

Acids and Acid Precursors

- Sulfur dioxide (SO_2) → sulfuric acid (H_2SO_4)
  - primarily from coal burning and smelting
- Nitrogen oxides (NO, NO_2) → nitric acid (HNO_3)
  - primarily from high-temperature combustion

strong acids

- Formic and acetic acids (HCO_2H, CH_3CO_2H)
  - primarily from biomass burning, mostly in Africa and South America
- Carbonic acid ($CO_2 \rightarrow H_2CO_3$)
  - from CO_2 in atmosphere, responsible for acidity of pristine precipitation

weak acids

Sources of Sulfur Dioxide (SO_2)

Anthropogenic

- Coal-burning in power plants
- Oil-burning (vehicles)
- Industrial (smelting, etc.); responsible for intense local damage
- Biomass burning

Natural

- volcanoes

SO_2 to Acid

- In water solution, sulfur dioxide dissolves in water to form sulfurous acid, which can go on to form sulfuric acid.

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$

$$H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O$$

- In the gas phase, sulfur dioxide can form sulfuric acid, H_2SO_4.

$$SO_2 + OH\cdot \rightarrow HOSO_2\cdot$$

$$HOSO_2\cdot + O_2 \rightarrow HO_2\cdot + SO_3$$

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$$

Sulfurous and Sulfuric Acid Ionizations

- Sulfuric acid and sulfurous acid form hydronium ions

$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$

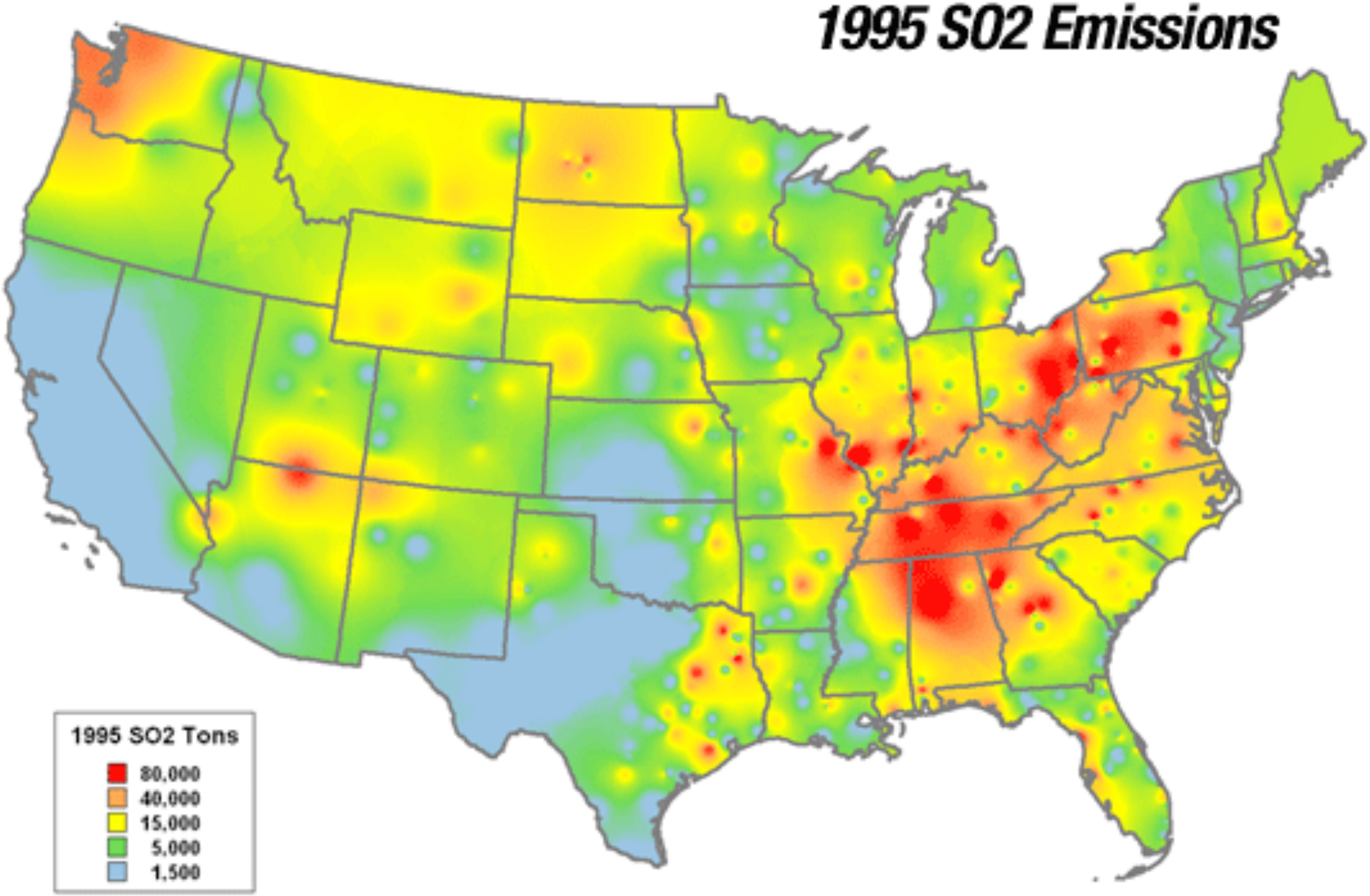
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$

$H_2SO_3 + H_2O \rightleftharpoons H_3O^+ + HSO_3^-$

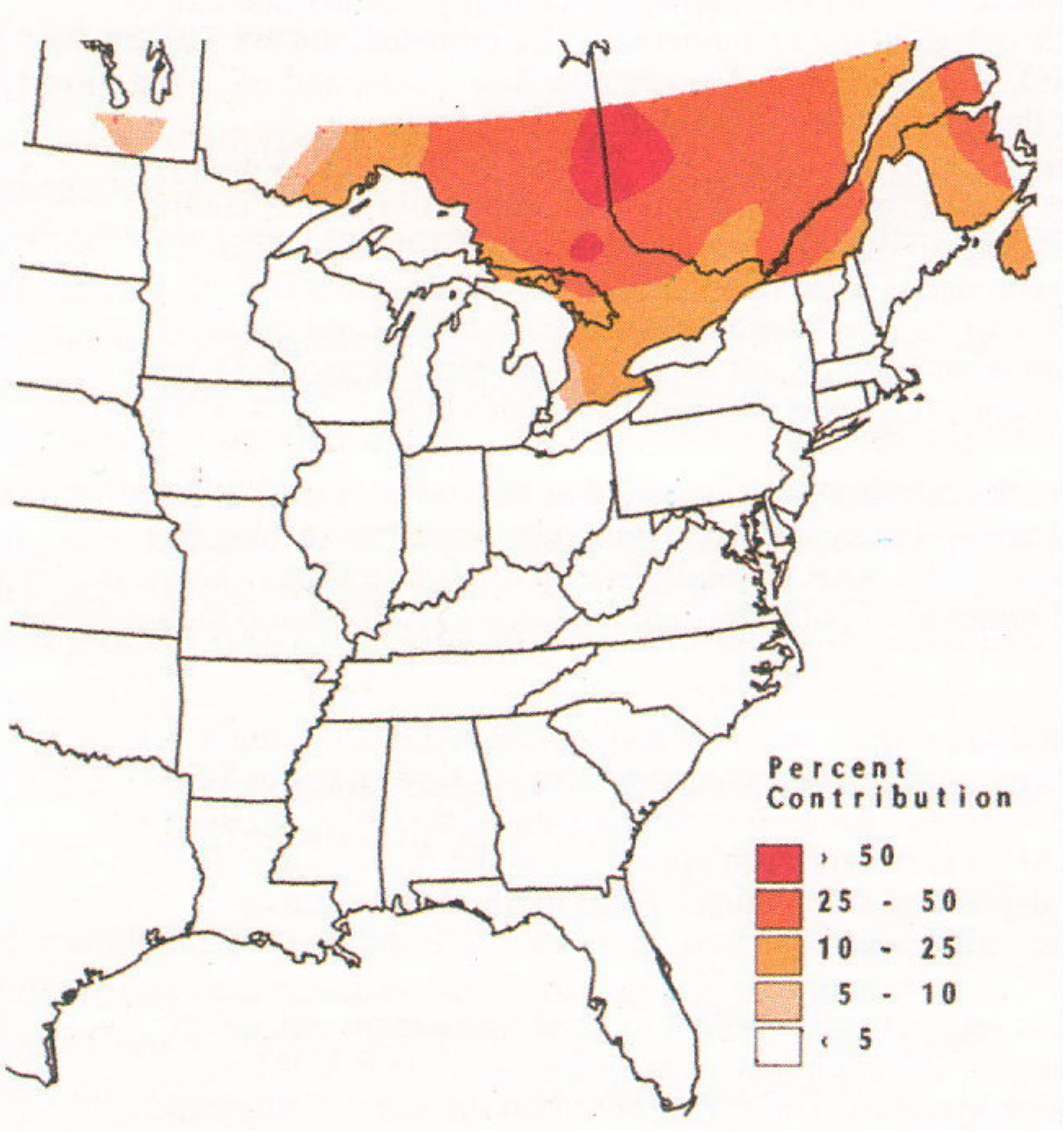
$HSO_3^- + H_2O \rightleftharpoons H_3O^+ + SO_3^{2-}$

- The pH can drop to 4.3 or lower.

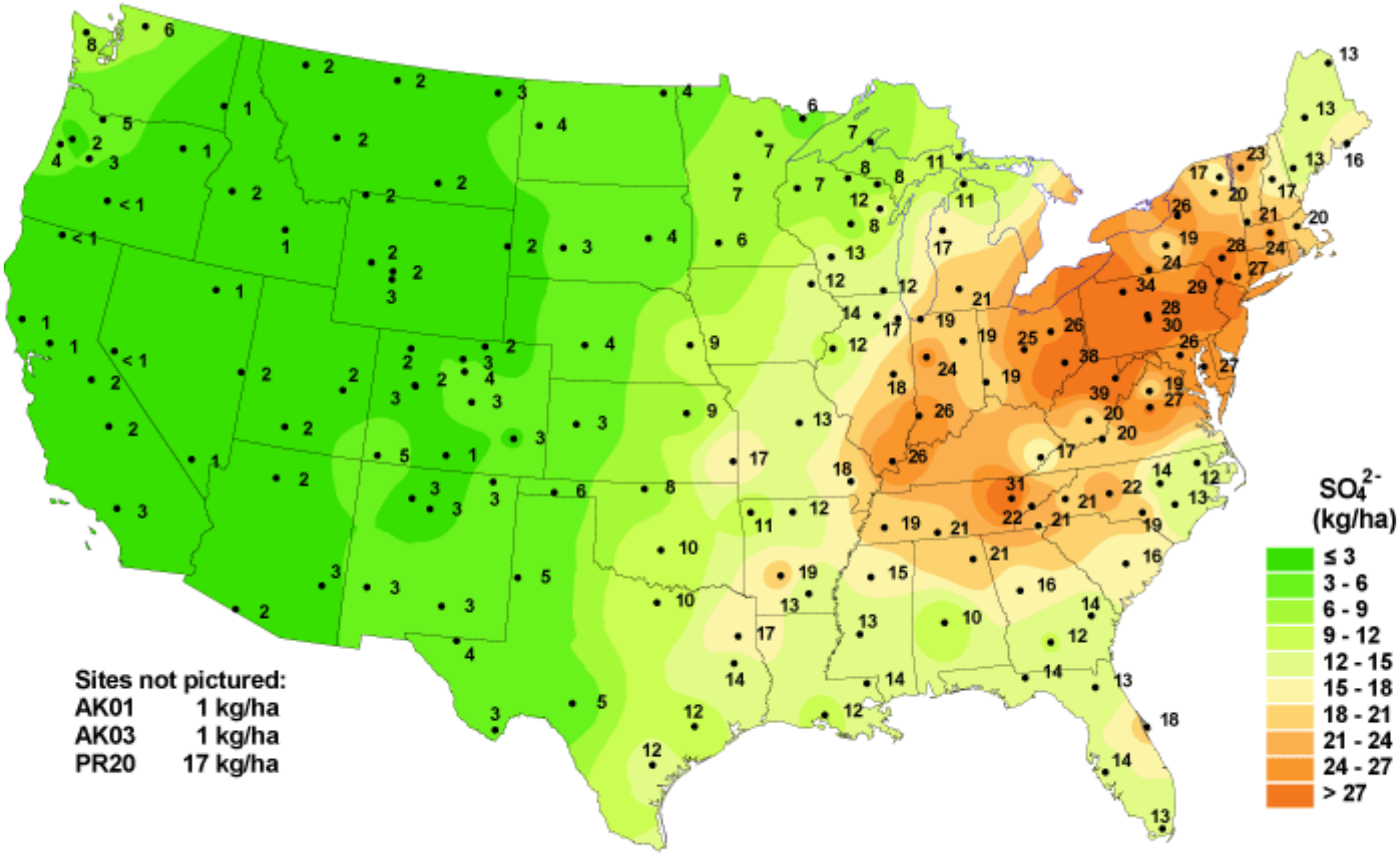
1995 SO2 Emissions



Contribution of U.S. Emissions to Total S Deposition in Canada



Wet Sulfate Deposition: 1994



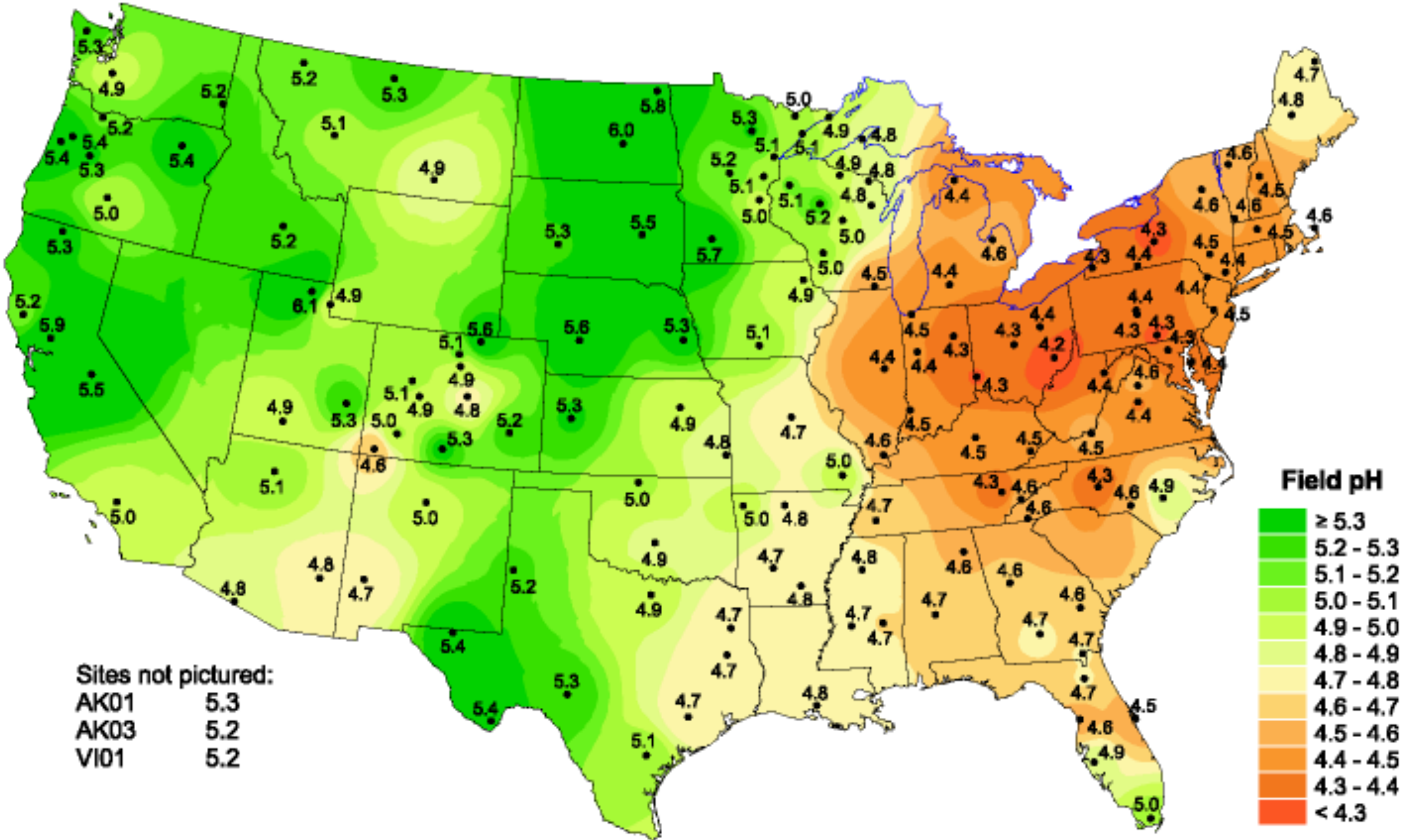
Sites not pictured:

AK01	1 kg/ha
AK03	1 kg/ha
PR20	17 kg/ha

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Average pH of Rainfall: 1999

Hydrogen ion concentration as pH from measurements made at the field laboratories, 1999



Sites not pictured:

AK01	5.3
AK03	5.2
VI01	5.2

National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Sources of Nitrogen Oxides (NOx)

Anthropogenic

- Fossil-fuels
    - vehicles (45% US)
    - power plants (35% US)
- Biomass burning
- Agricultural soils

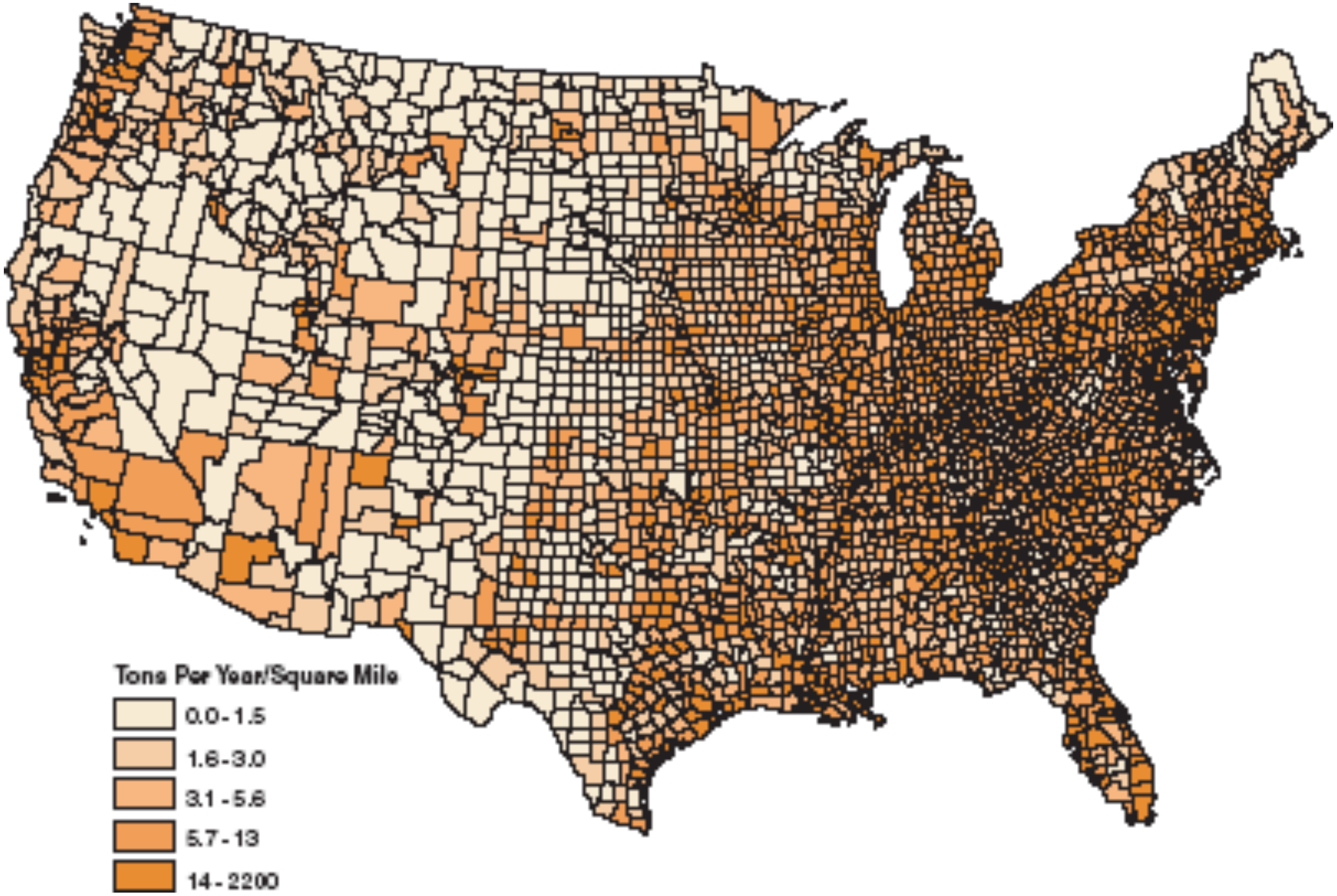
Natural

- Lightning
- Soils

NO_x is NO and NO_2

- Combustion and other high-temp processes in air (O_2 + N_2) produce NO and NO_2; together they are referred to as “nitrogen oxides” or “NOx”
- 95% of NOx from combustion sources is emitted in the form of NO, but this is quickly oxidized in the atmosphere to NO_2, and so emissions of NOx can be reported as t(NO_2).

NO$_2$ Emission Density: 2001



Nitric Acid Formation

- Nitric acid formation in gas phase

  $NO_2 + OH\cdot \rightarrow HNO_3$

- HNO_3 formation in water solution

  $3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$

- Nitrogen monoxide will oxidize to form nitrogen dioxide that again reacts with water, ultimately forming nitric acid:

  $4\ NO + 3\ O_2 + 2\ H_2O \rightarrow 4\ HNO_3$

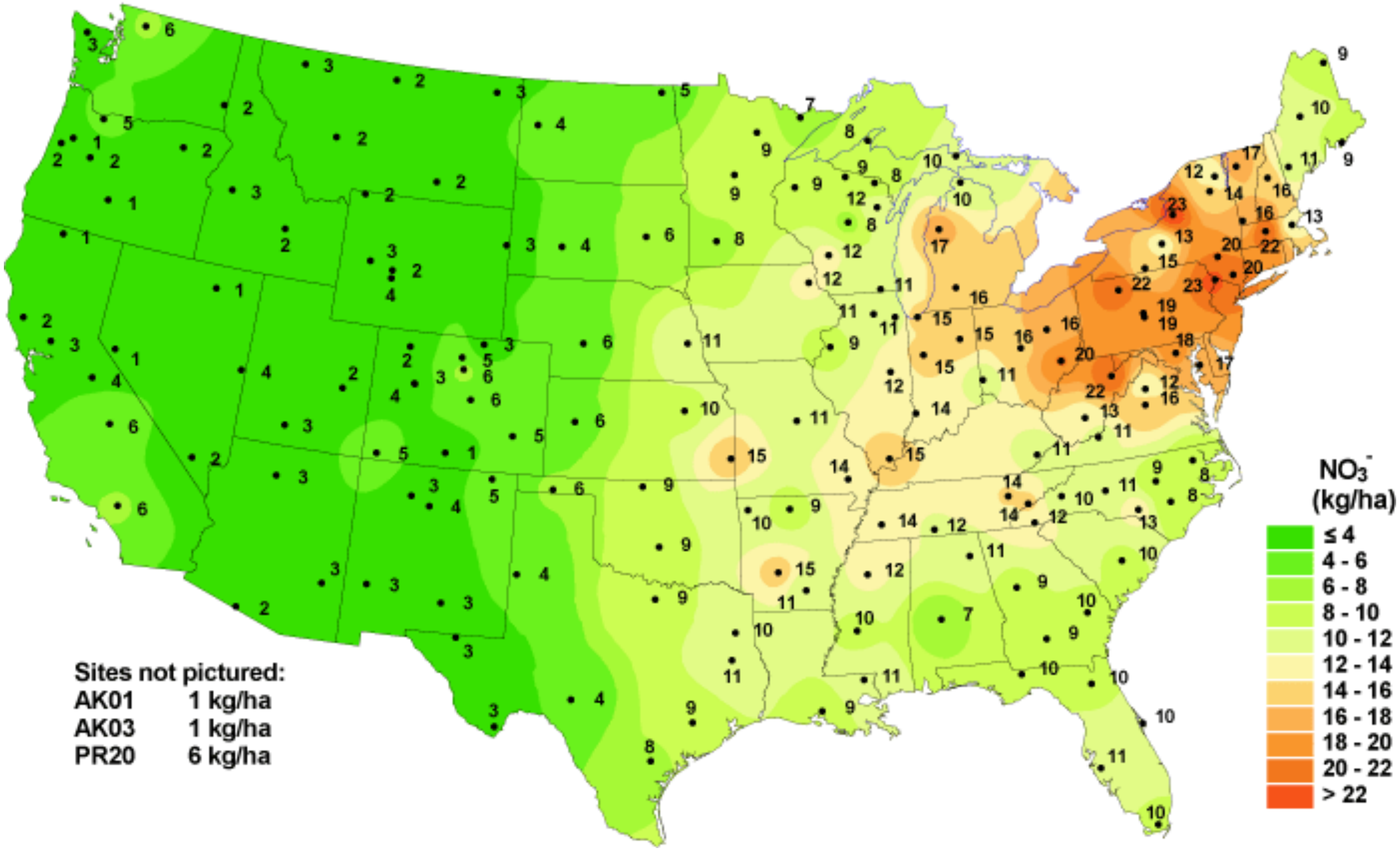
- Nighttime

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M^*$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

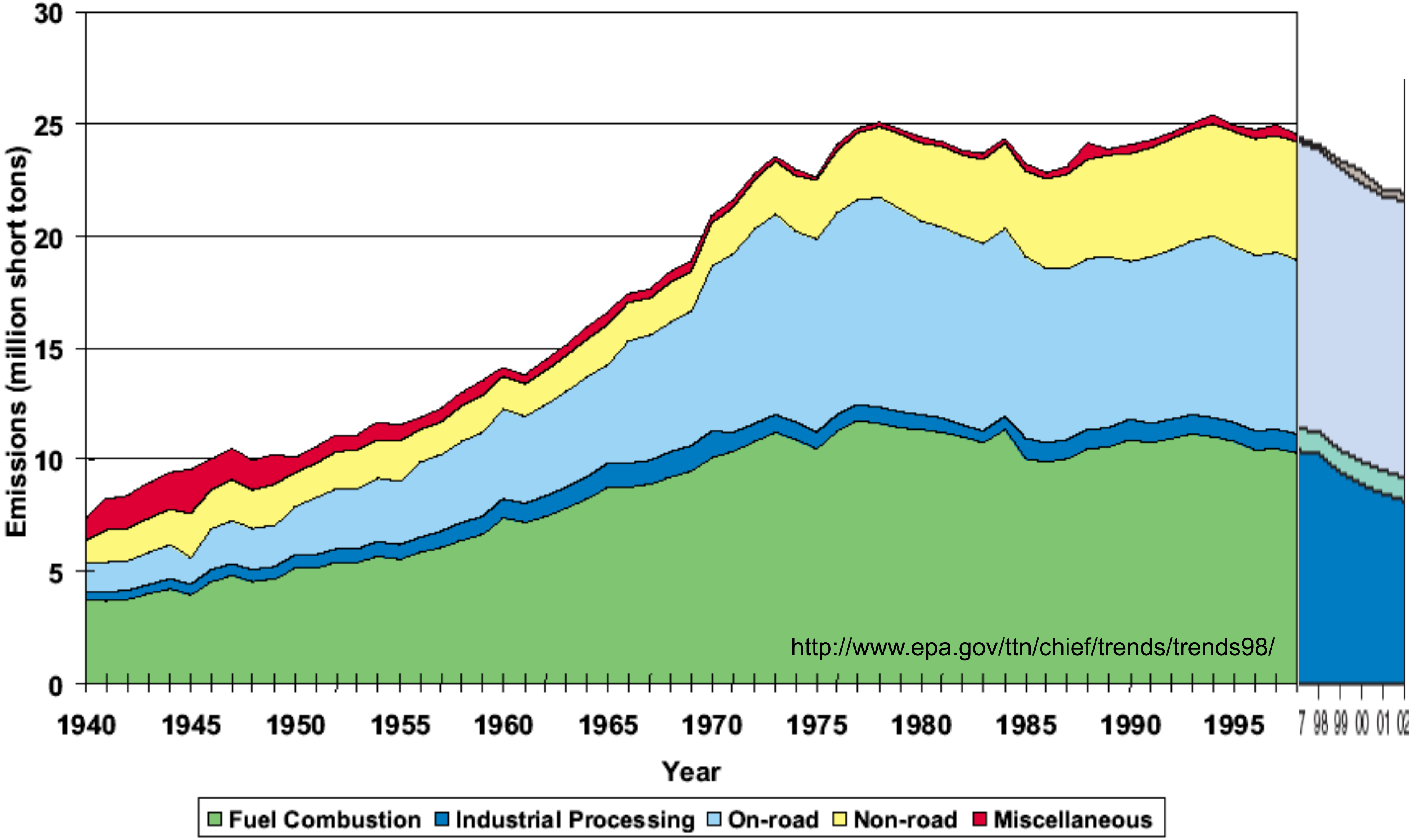
Wet Nitrate Deposition: 1994



Sites not pictured:

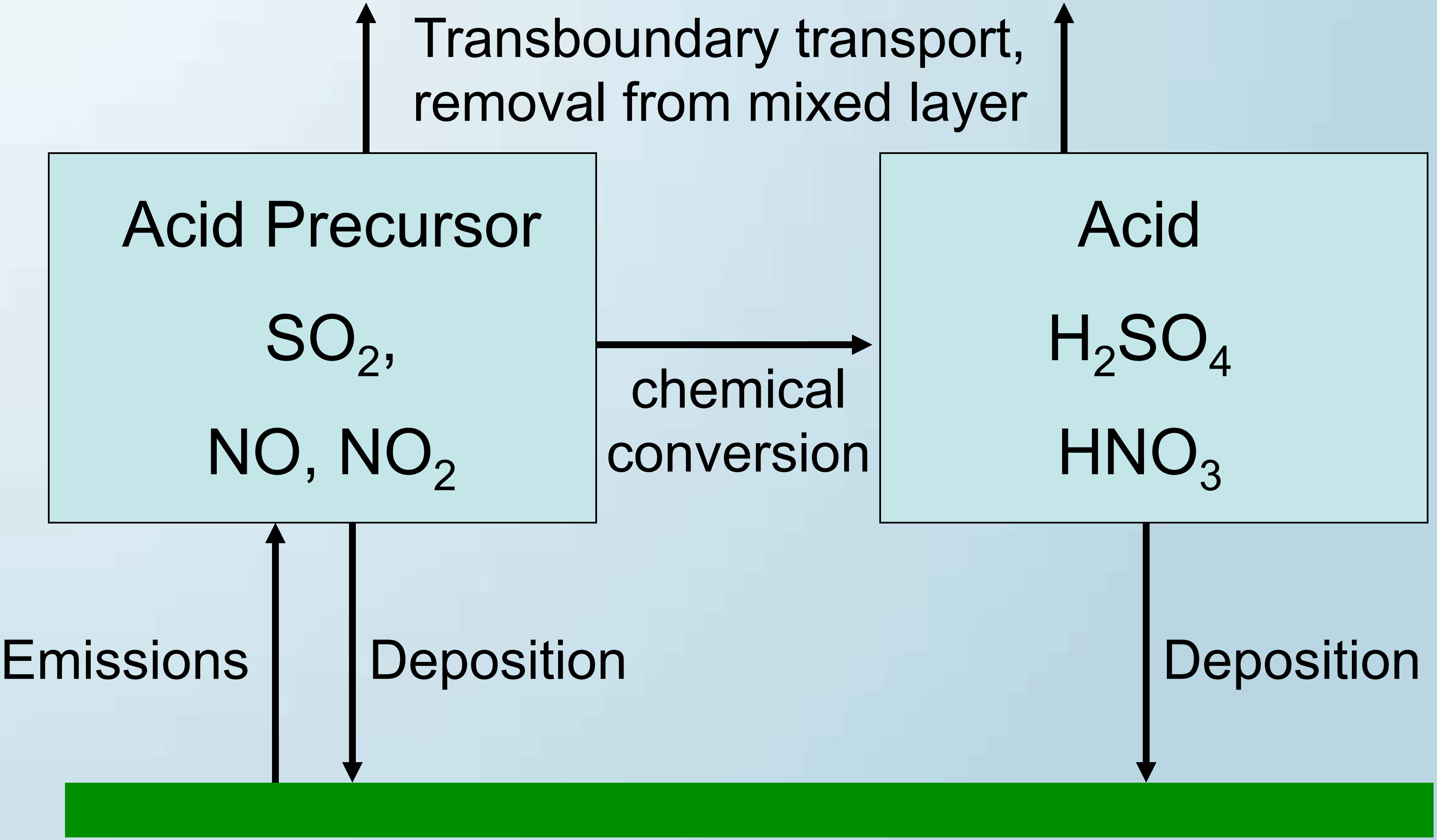
AK01	1 kg/ha
AK03	1 kg/ha
PR20	6 kg/ha

US NO$_2$ Emissions, 1940-2002



http://www.epa.gov/ttn/chief/trends/trends98/

Transport, Conversion, Deposition



Transboundary transport, removal from mixed layer

Acid Precursor

SO_2,

NO, NO_2

chemical conversion

Acid

H_2SO_4

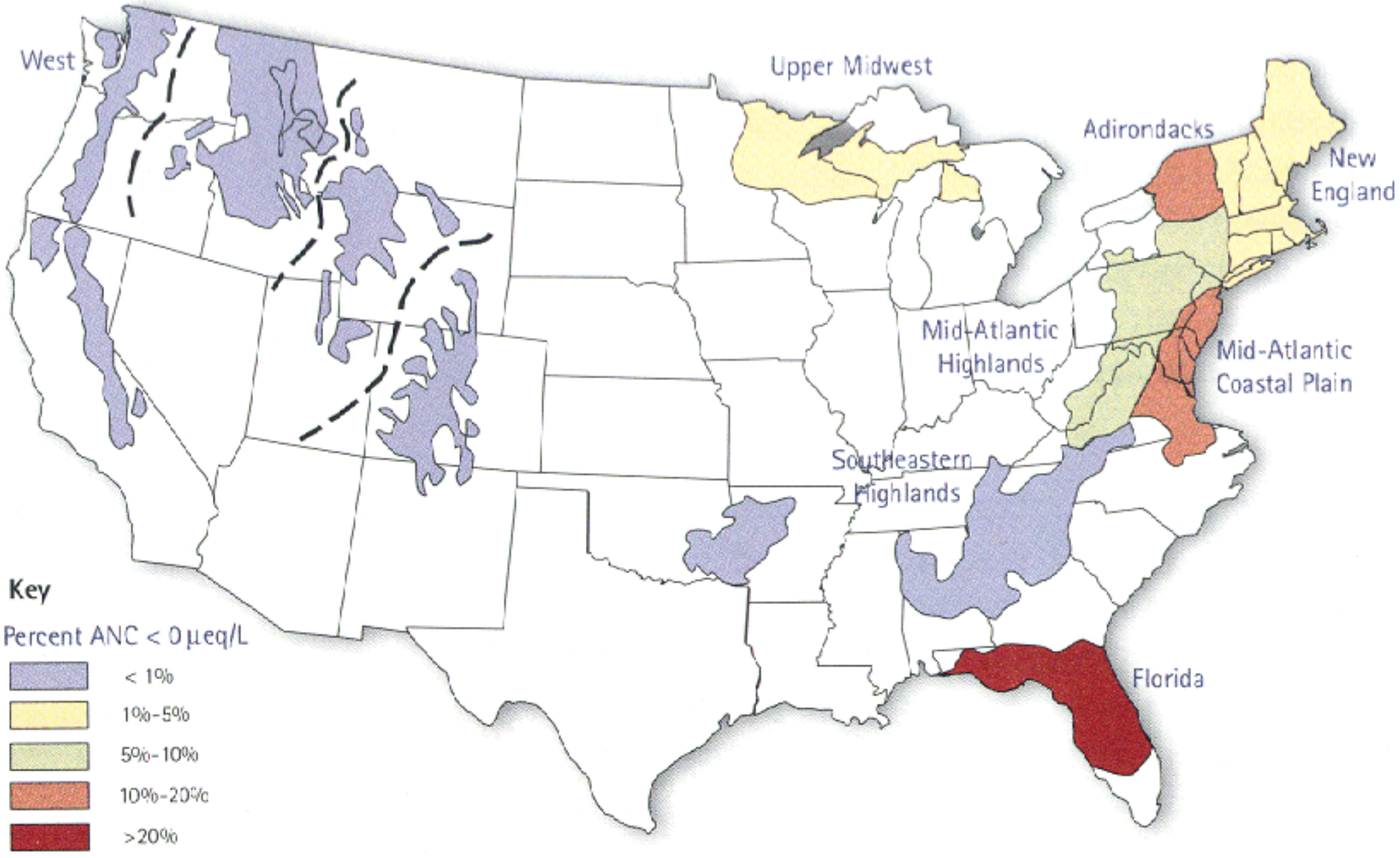
HNO_3

Emissions

Deposition

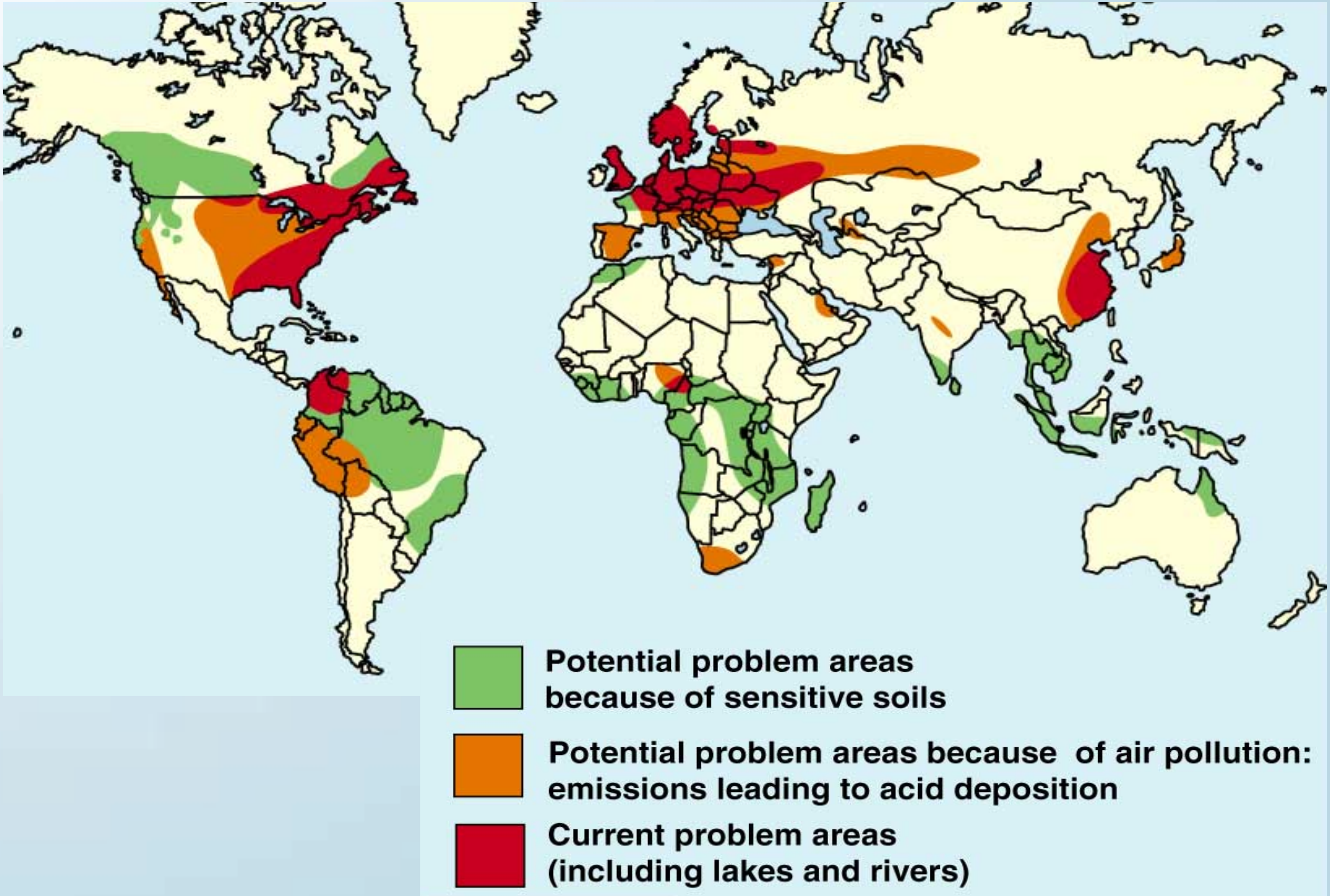
Deposition

Sensitive Areas



Source: NAPAP. 1991. 1990 Integrated Assessment Report.

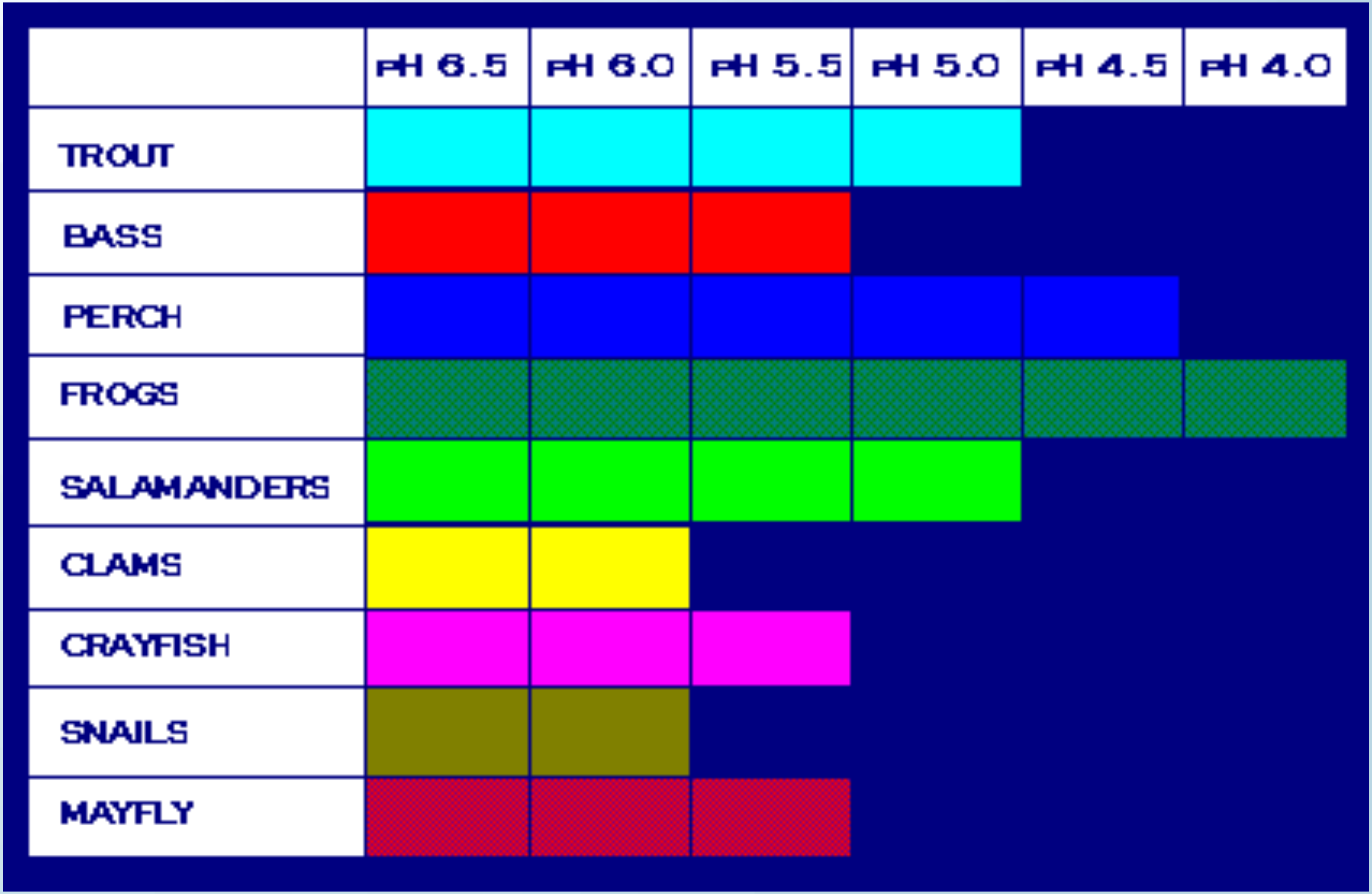
Sensitive Areas



Impacts

- Freshwater ecosystems
- Forests
- Agriculture
- Human health
- Buildings and property
- Visibility

Acid Tolerance of Freshwater Animals



	pH 6.5	pH 6.0	pH 5.5	pH 5.0	pH 4.5	pH 4.0
TROUT	■	■	■	■		
BASS	■	■	■			
PERCH	■	■	■	■	■	
FROGS	■	■	■	■	■	■
SALAMANDERS	■	■	■	■		
CLAMS	■	■				
CRAYFISH	■	■	■			
SNAILS	■	■				
MAYFLY	■	■	■			

Forests and Acid Rain

Human Health

- Acids
  - Consumption of fish with elevated concentrations of toxic metals (Al, Pb, Cd, Hg, Cu, Zn)
  - Corrosion of pipes resulting in excess levels of Cu, Zn, Pb
    - In Adirondacks, Pb levels up to 100× standard
- Acid precursors
  - SO_2 and NO_x are toxic;
  - NO_x react to form ozone
  - Respiratory and cardiac diseases

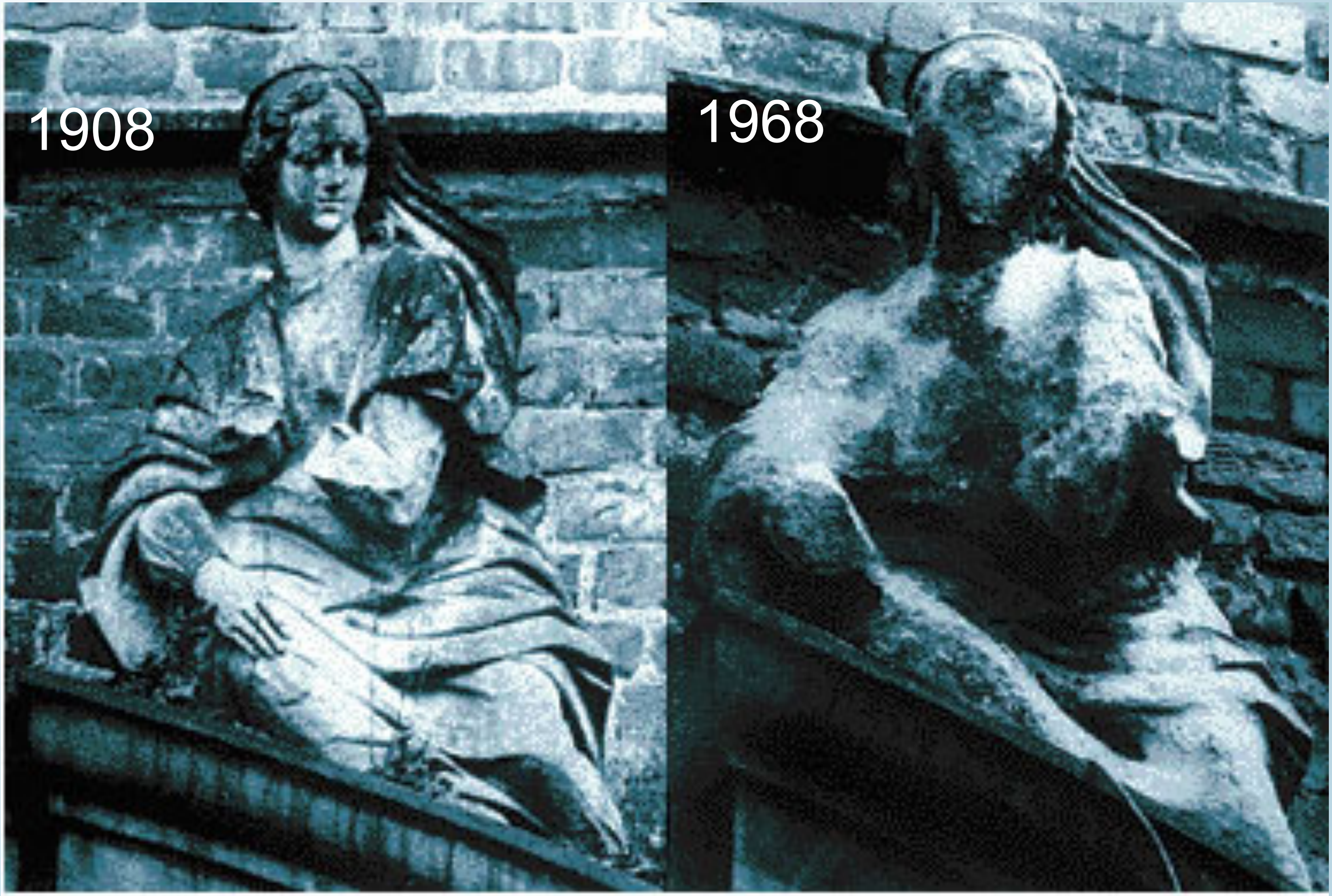
Buildings and Property

- Carbonate stones (marble, limestone, etc.), cement, mortar are dissolved by acids:

$$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + CO_2(g) + H_2O(l)$$

- Acids etch glass; damage roofing and other building materials; damage plastics and paint (esp. automotive paint)
- Damage to U.S. buildings: ≈$5 billion/y

Capitol Building, Ottawa



Jefferson Memorial

Marble surfaces develop a rough "sugary" texture because calcite grains are loosened as the edges dissolve

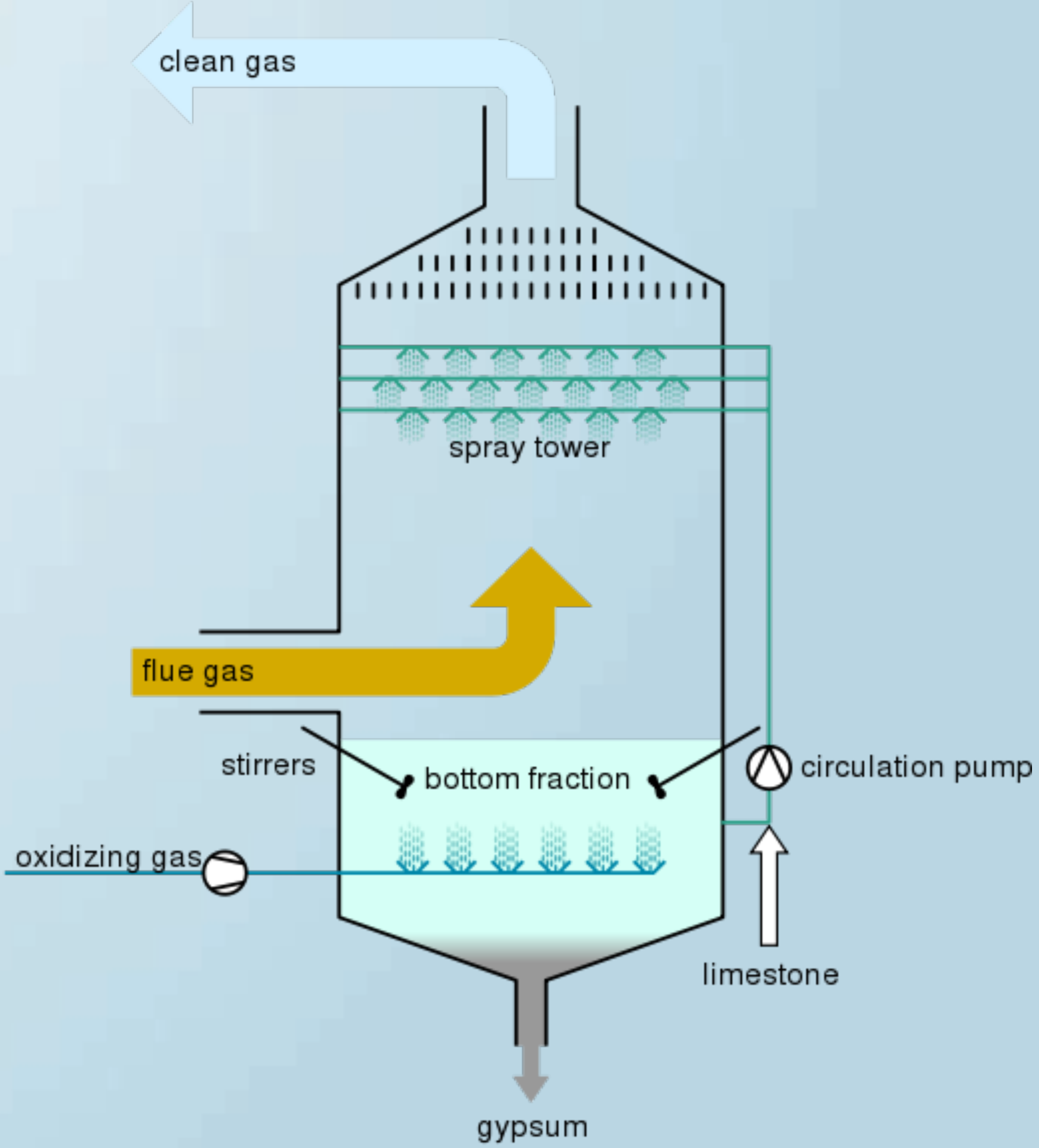
Effects on Metals

Mitigation

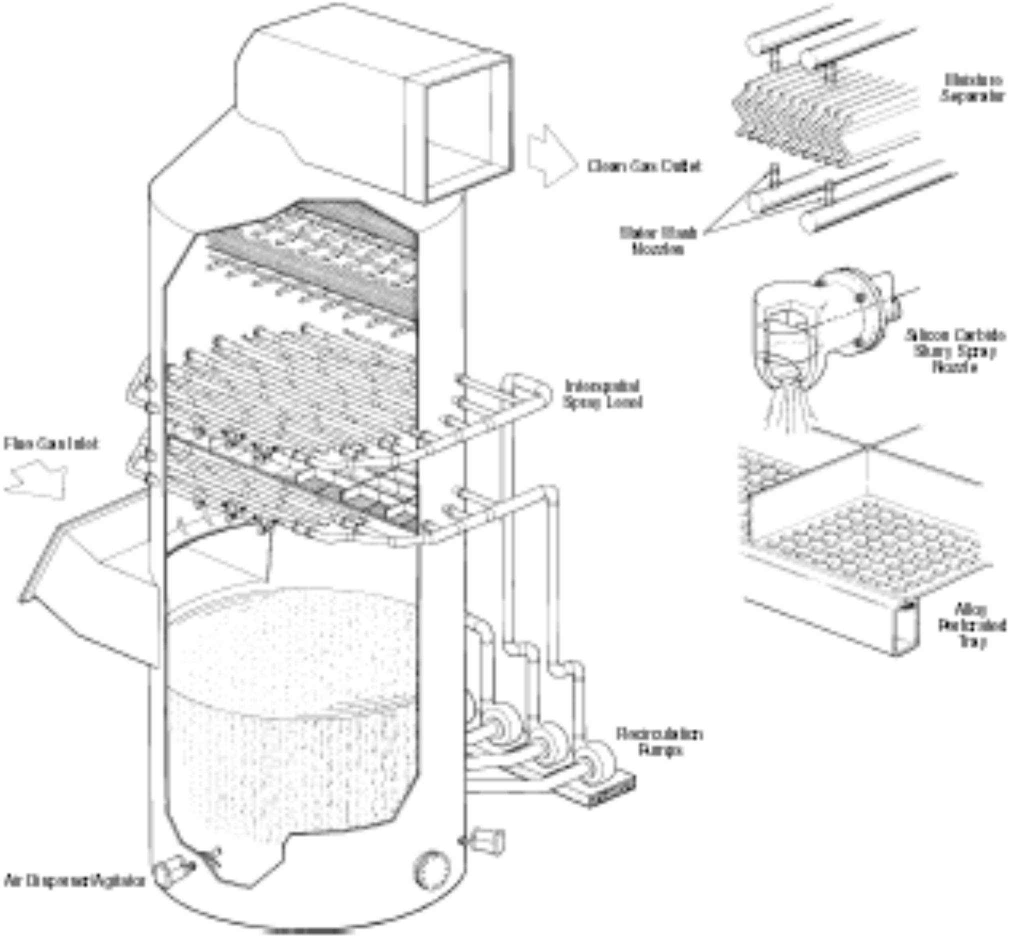
- Tall Stacks (export pollution)
- Sulfur
  - Switch from coal to natural gas (0.001% S)
  - Switch to low-sulfur coal
    - S content ranges from 0.3 to 6%; only 8% of US coal would meet 1975 NSPS (<0.7% S)
  - Scrub coal (solvent refining removes up to 75% S)
  - Flue-gas desulfurization (FGD)
    - mix exhaust gas with lime (CaO); SO_2 reacts for form gypsum ($CaSO_4$)

SO_2 Emissions Reduction

- Due largely to the US EPA's Acid Rain Program, the U.S. had a 33% decrease in SO_2 emissions between 1983 and 2002.
- Partly from flue-gas desulfurization.



Wet SO_2 Scrubber



Flue-Gas Desulfurization

- A technology that enables SO_2 to be removed in power plants burning sulfur-containing coal or oil.
- Wet scrubbing uses a $CaCO_3$ (limestone) slurry and produces $CaSO_3$ (calcium sulfite):

  $CaCO_3(s) + SO_2(g) \rightarrow CaSO_3(s) + CO_2(g)$
- When wet scrubbing with a $Ca(OH)_2$ (lime) slurry, the reaction also produces $CaSO_3$ is:

  $Ca(OH)_2(s) + SO_2(g) \rightarrow CaSO_3(s) + H_2O(l)$
- When wet scrubbing with a $Mg(OH)_2$, the reaction produces $MgSO_3$:

  $Mg(OH)_2(s) + SO_2(g) \rightarrow MgSO_3(s) + H_2O\ (l)$
- To partially offset the cost of the FGD installation, in some designs, the $CaSO_3$ is further oxidized to produce marketable $CaSO_4 \cdot 2H_2O$ (gypsum).

  $CaSO_3(s) + \frac{1}{2}O_2(g) \rightarrow CaSO_4(s)$

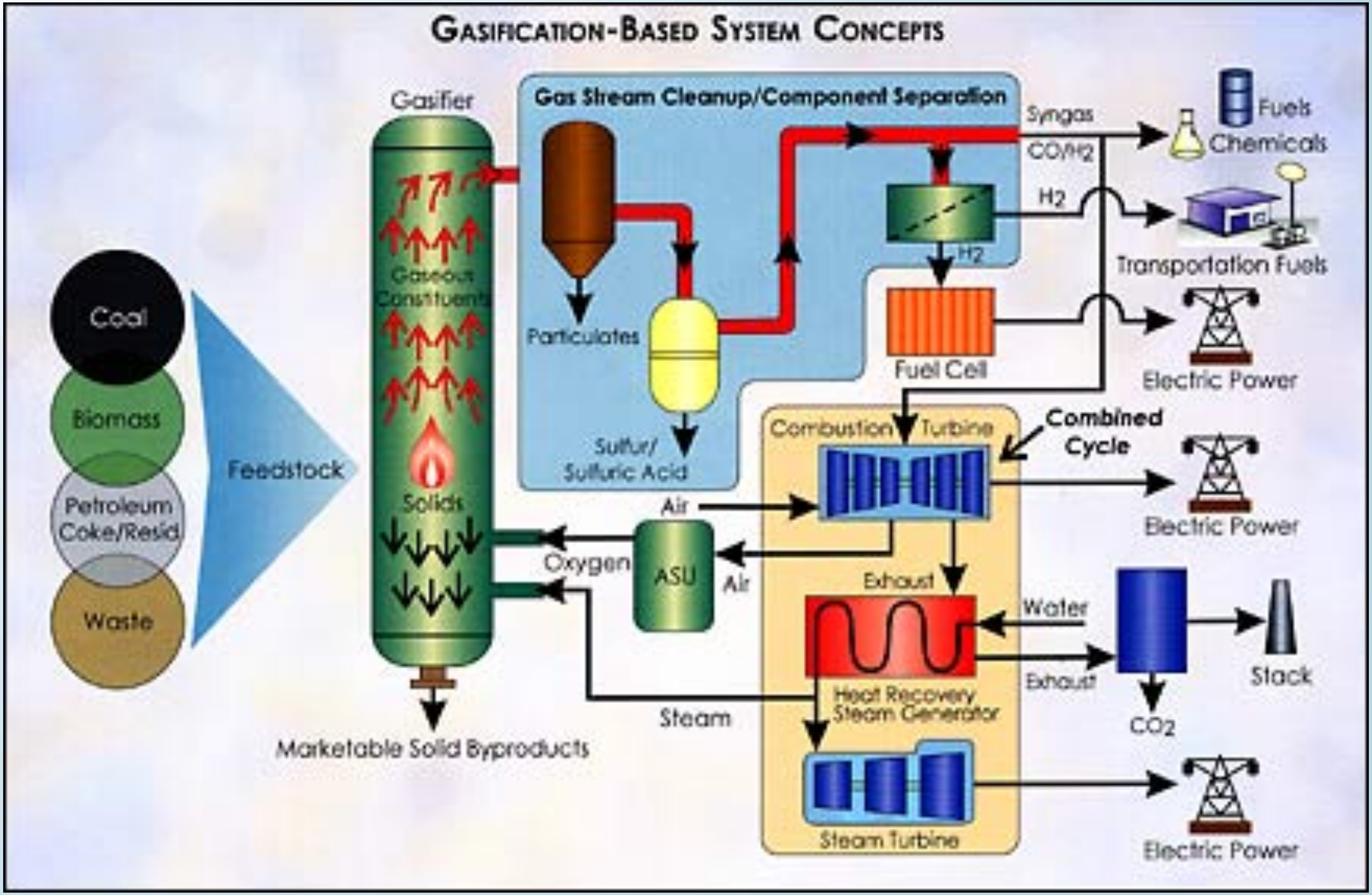
Mitigation – Coal Gasification

- A gasifier converts hydrocarbon feedstock into gaseous components by applying heat under pressure in the presence of steam.
- Only a relatively small portion of the fuel burns completely. This "partial oxidation" process provides the heat.
- Produce "syngas”, primarily hydrogen and carbon monoxide

  $C + H_2O \rightarrow CO + H_2$

  $CO + H_2O \rightarrow CO_2 + H_2$
- Sulfur converted to hydrogen sulfide, H_2S, and carbonyl sulfide, OCS, which can be converted into elemental sulfur or sulfuric acid, both valuable byproducts.
- 99+% of S removed

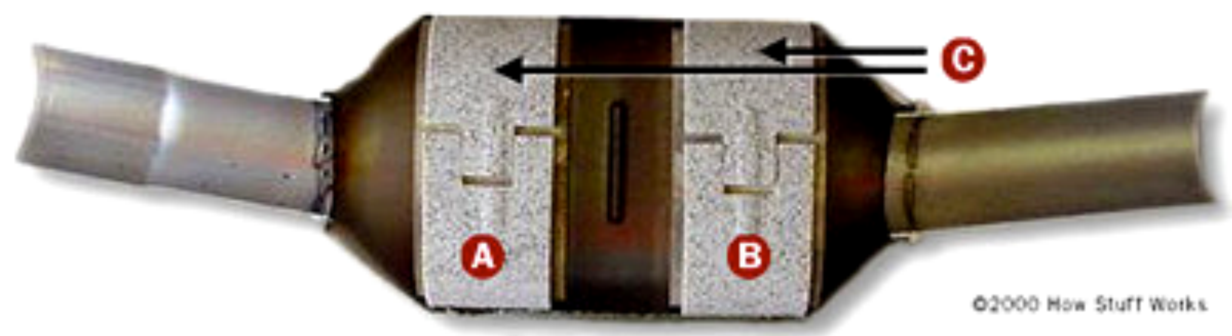
Coal Gasification



Automobile Catalytic Converters

Catalytic converters: up to 95% reduction in NO_x

$2NO \rightarrow N_2 + O_2$ $2NO_2 \rightarrow N_2 + 2O_2$



A Reduction catalyst
B Oxidation catalyst
C Honeycomb

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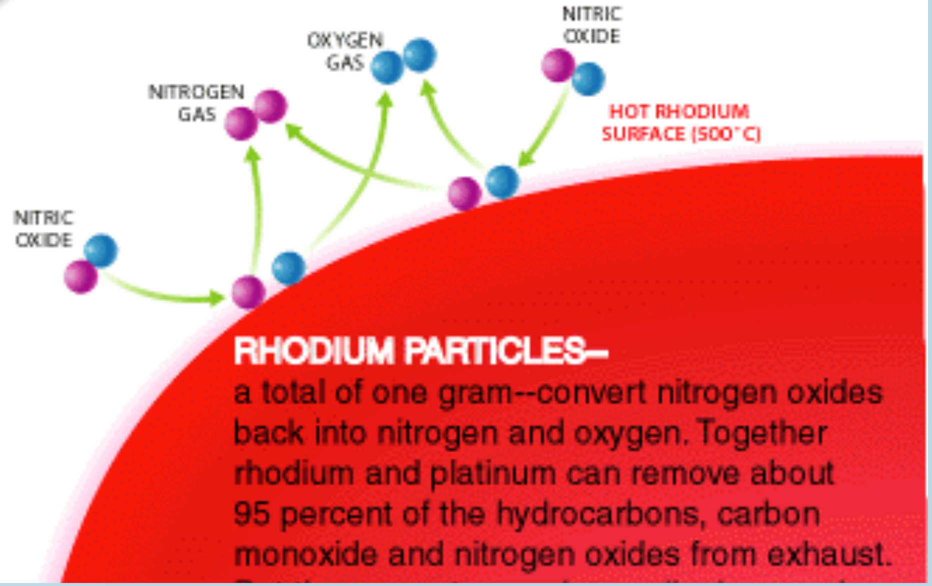
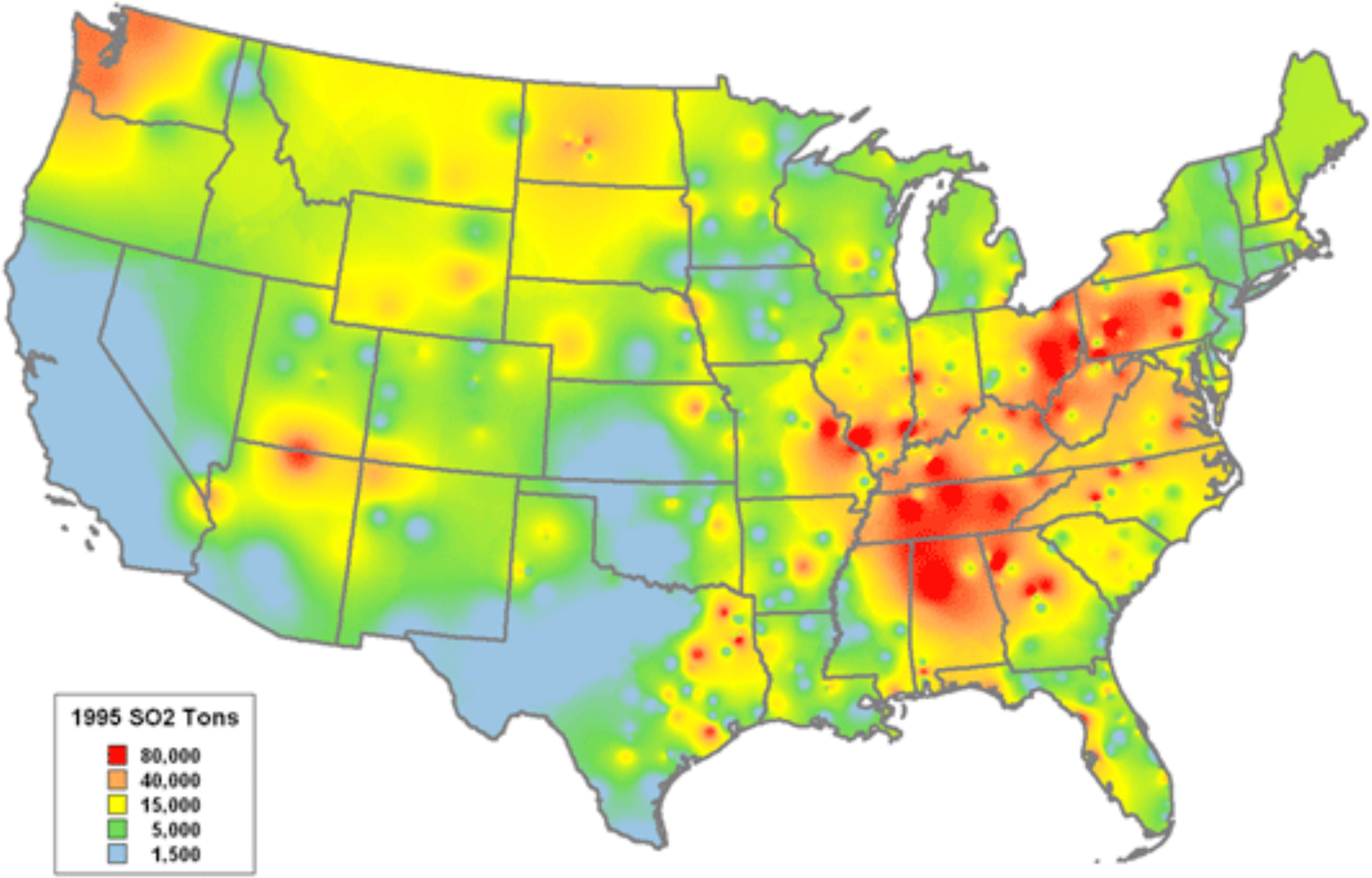
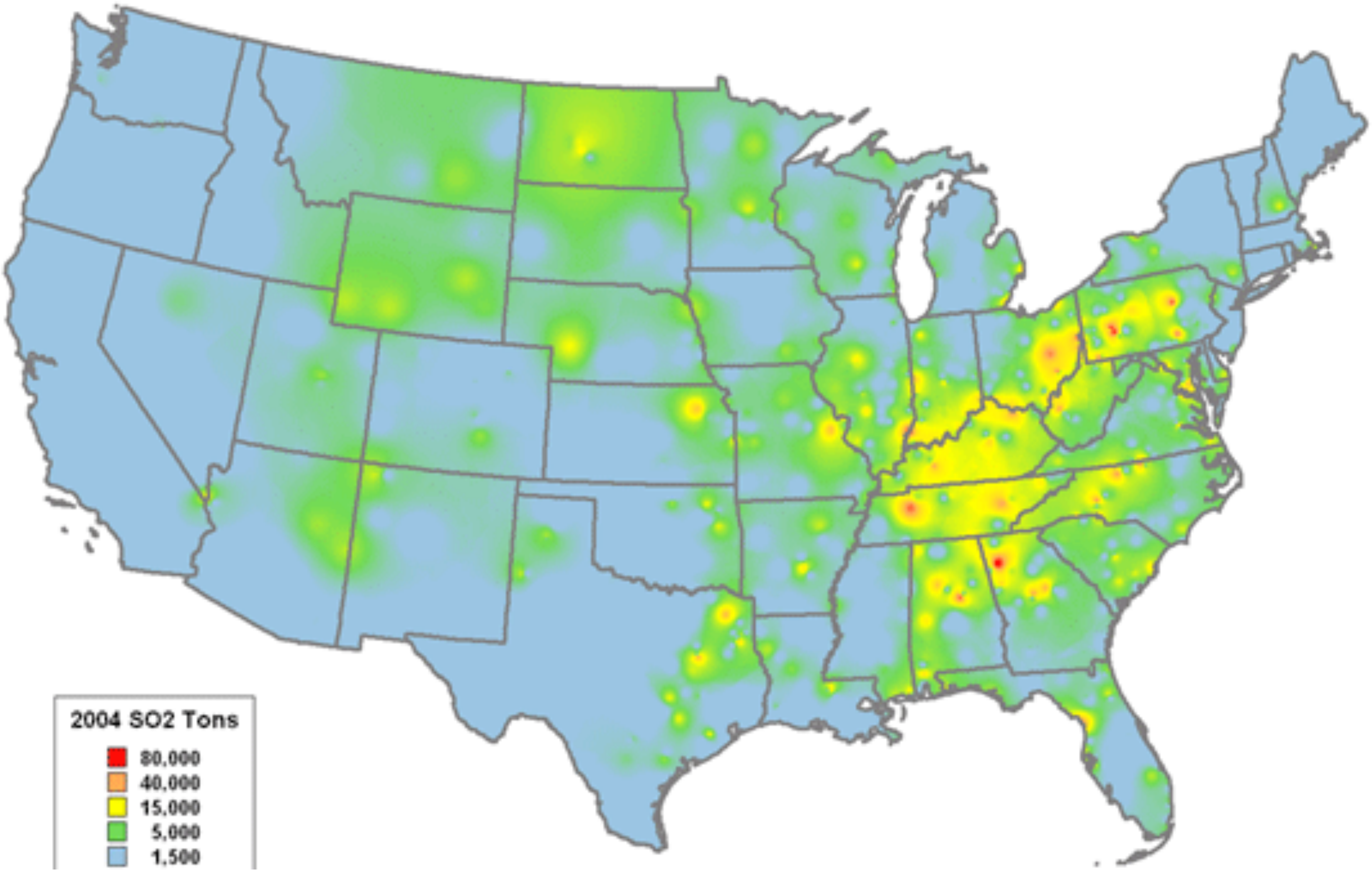


RHODIUM PARTICLES–
a total of one gram--convert nitrogen oxides back into nitrogen and oxygen. Together rhodium and platinum can remove about 95 percent of the hydrocarbons, carbon monoxide and nitrogen oxides from exhaust.

1995 SO_2 Emissions



2004 SO_2 Emissions

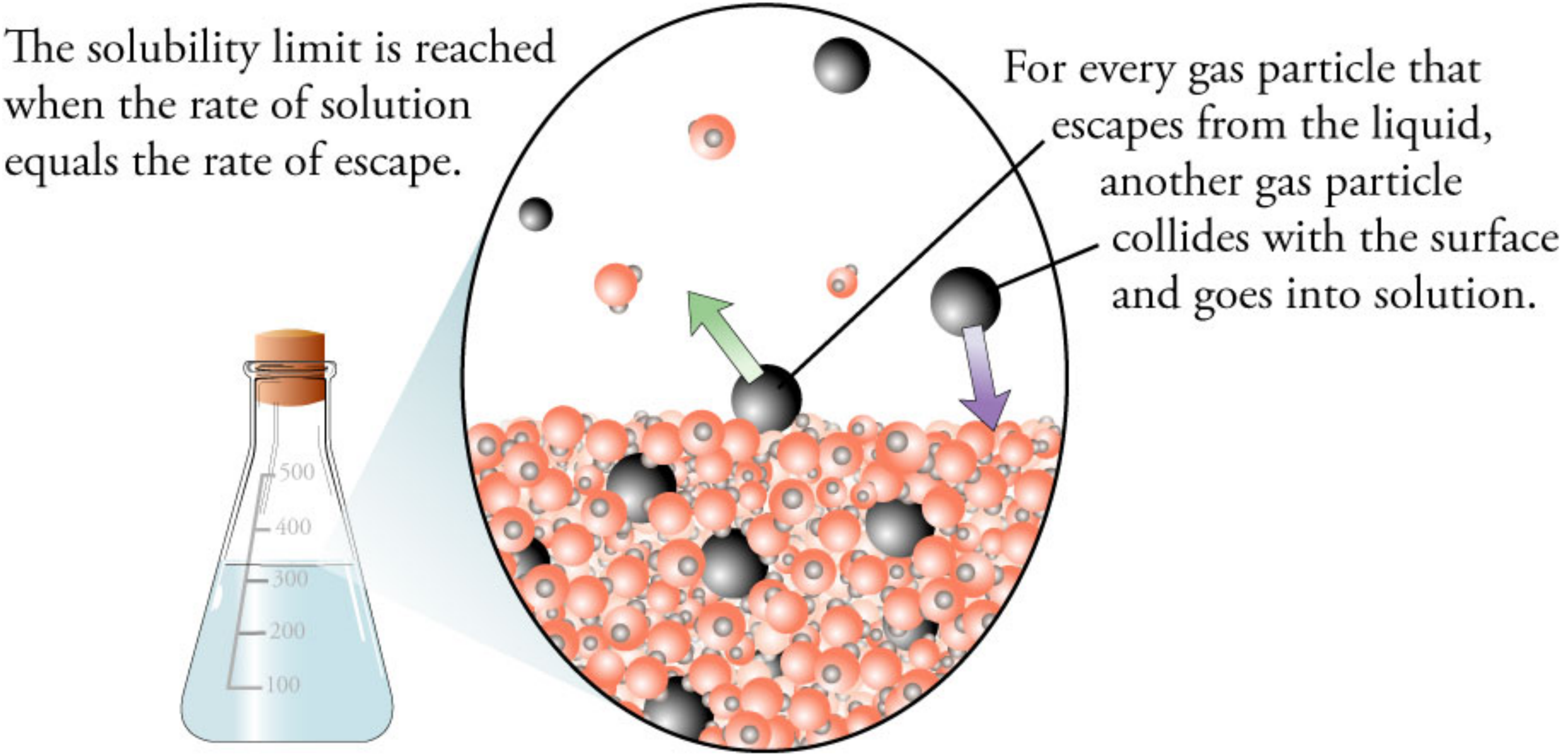


Oceanic Carbon

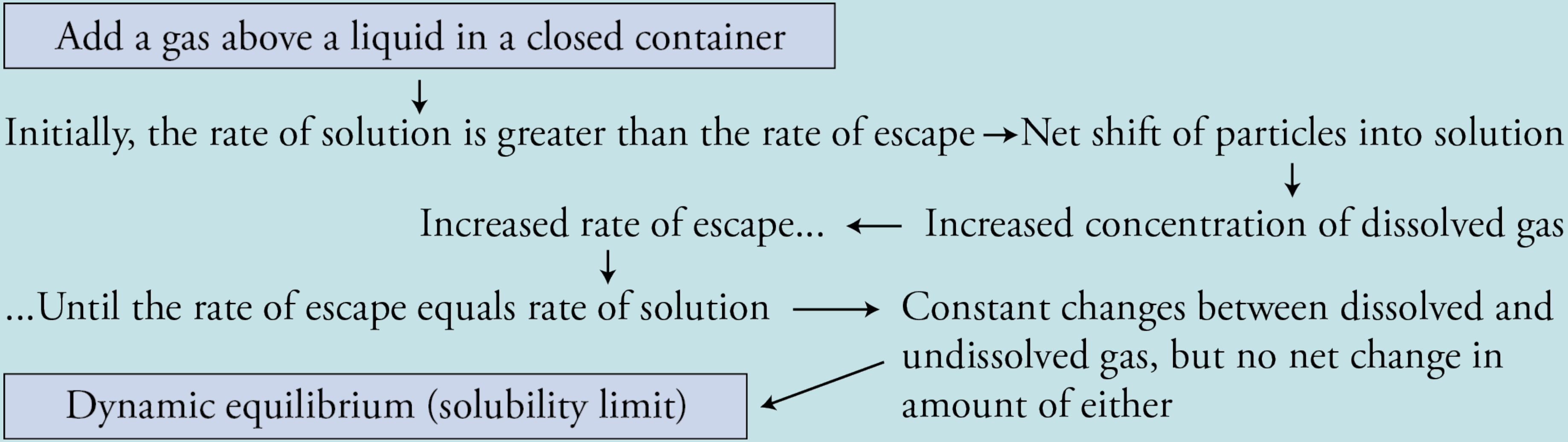
- Carbon enters the ocean mainly through solution of atmospheric carbon dioxide.

  $CO_2(g) \rightleftharpoons CO_2(aq)$
- The net rate of solution is determined by
  - the rate at which CO_2 molecules collide with the surface of the water and move into the water (R_{soln})
  - the rate at which CO_2 escapes from the water into the atmosphere (R_{escape}) , which is determined by the concentration of CO_2 in the water and the temperature of the water.
- If these two rates are equal, the system will be in equilibrium with no net change in the concentrations of CO_2 in the ocean or the atmosphere.

Dynamic Equilibrium for Gas Dissolved in Liquid



Gas Solubility



Add a gas above a liquid in a closed container

↓

Initially, the rate of solution is greater than the rate of escape → Net shift of particles into solution

↓

Increased rate of escape… ← Increased concentration of dissolved gas

↓

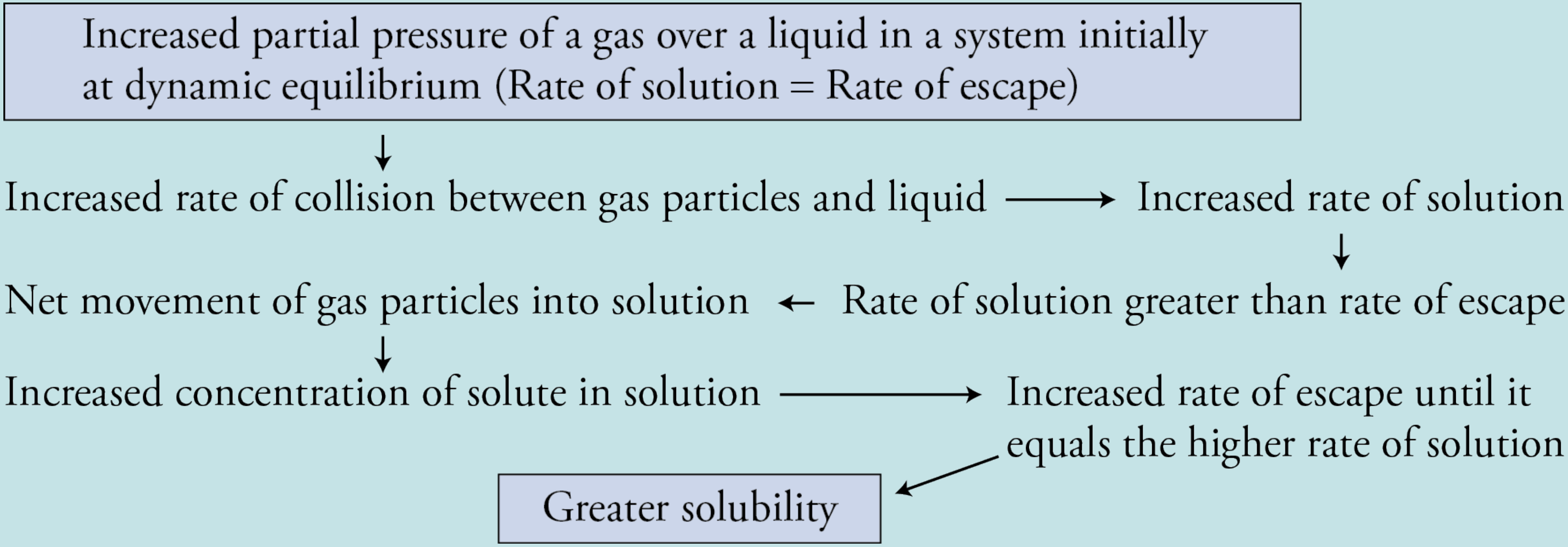
…Until the rate of escape equals rate of solution → Constant changes between dissolved and undissolved gas, but no net change in amount of either

↙

Dynamic equilibrium (solubility limit)

Partial Pressure and Gas Solubility

- As the concentration of CO_2 in the atmosphere increases, the ocean absorbs more CO_2.
- Increased concentration of CO_2 in the atmosphere leads to an increase in the rate of collisions with the ocean, increasing the rate of solution, disrupting the dynamic equilibrium, making the $R_{soln} > R_{escape}$, and leading to a net shift of CO_2 into the ocean.



Increased partial pressure of a gas over a liquid in a system initially at dynamic equilibrium (Rate of solution = Rate of escape)

Increased rate of collision between gas particles and liquid

Increased rate of solution

Rate of solution greater than rate of escape

Net movement of gas particles into solution

Increased concentration of solute in solution

Increased rate of escape until it equals the higher rate of solution

Greater solubility

CO_2 and Ocean Acidity

- CO_2 molecules react with water to form carbonic acid, which ionizes to form hydronium, hydrogen carbonate, and carbonate ions.

  $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

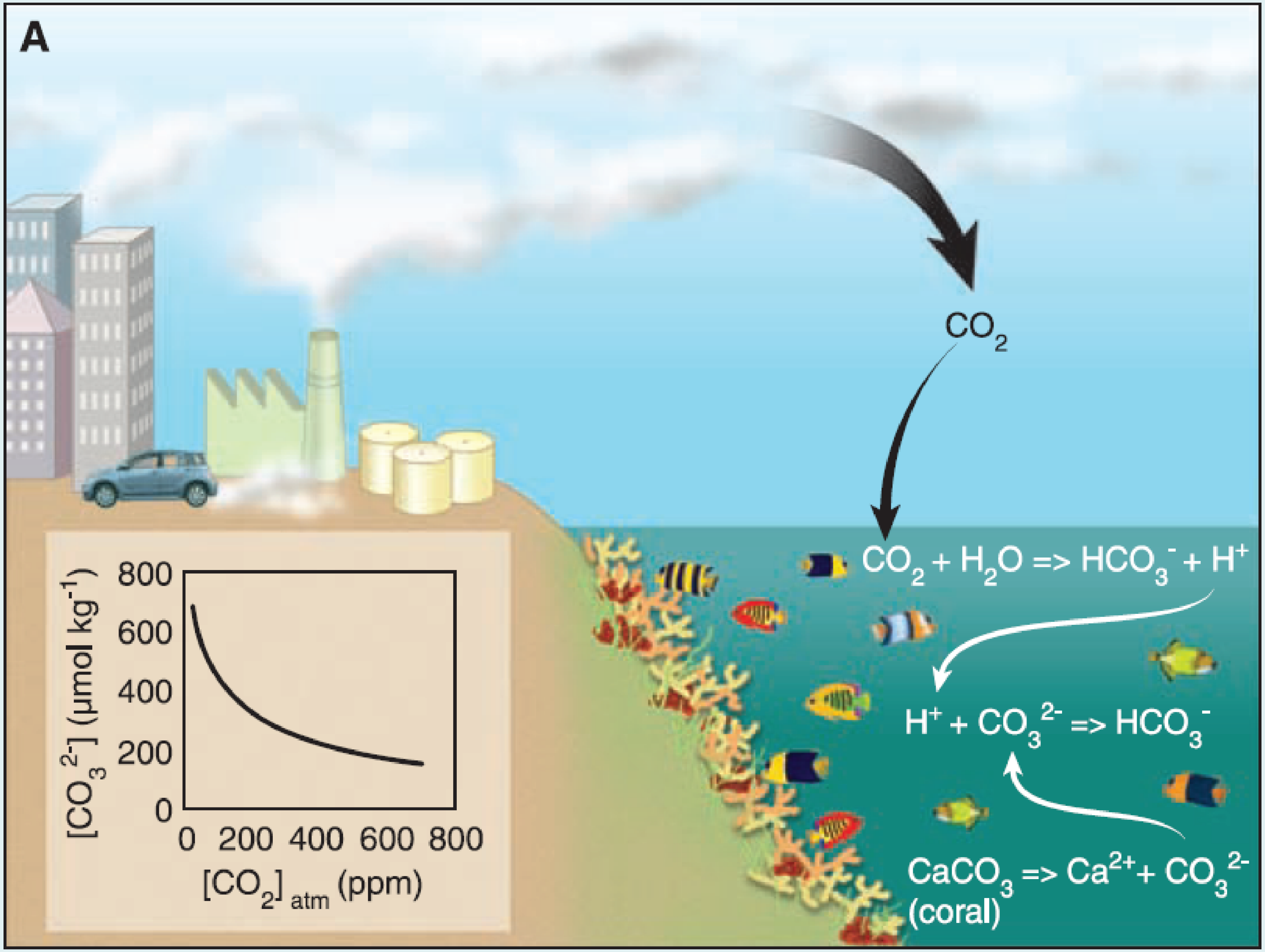
  $H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$

  $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$

- The absorption of anthropogenic CO_2 has acidified the surface layers of the ocean, with a steady decrease of 0.02 pH units per decade over the past 30 years and an overall decrease since the pre-industrial period of 0.1 pH units.
- Although these increases appear small in terms of pH, they are associated with a substantial changes in ocean chemistry.

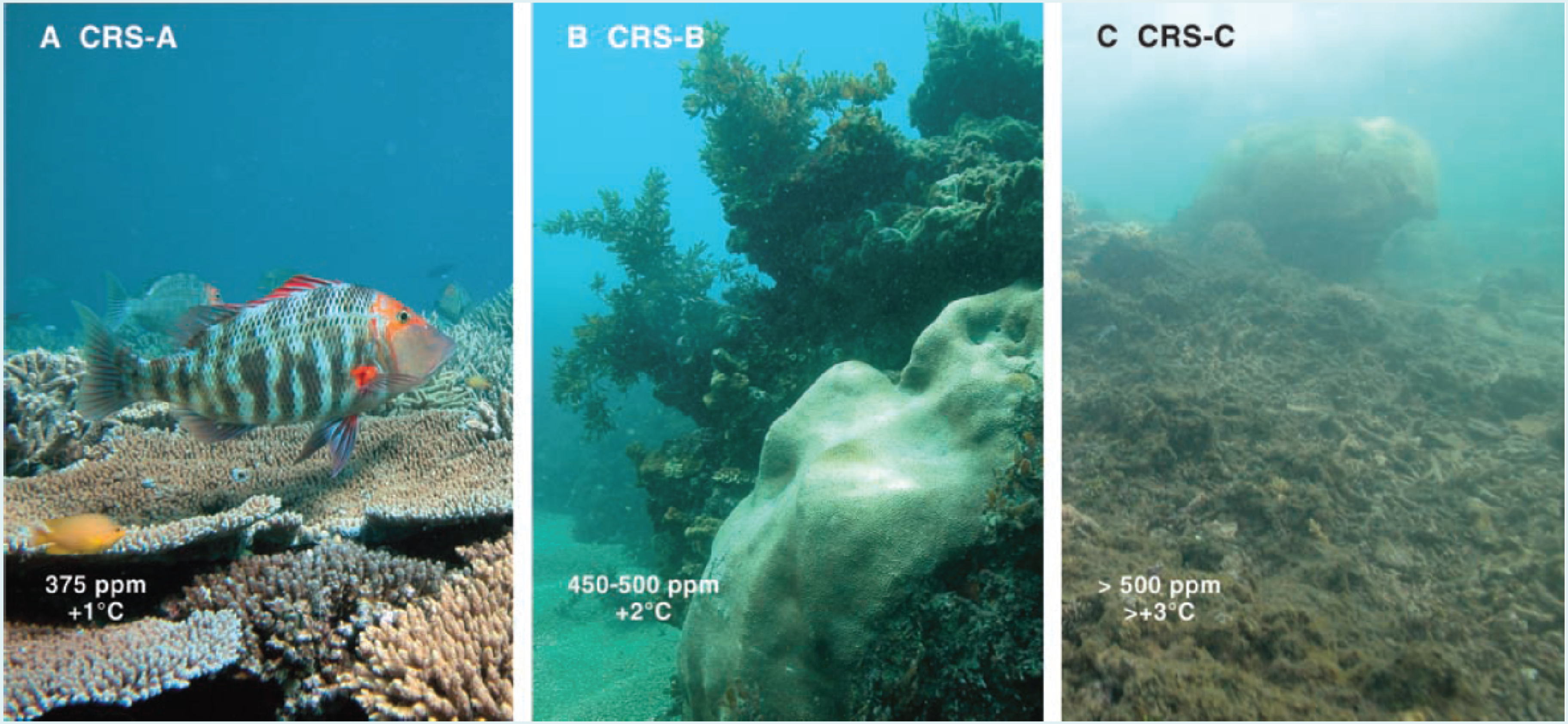
O Hoegh-Guldberg, J F Bruno Science 2010;328:1523-1528

Threat to Coral Reefs



Coral Reefs Under Rapid Climate Change and Ocean Acidification
Ove Hoegh-Guldberg, et al, *Science 14 December 2007: Vol. 318 no. 5857 pp. 1737-1742*

Threat to Coral Reefs



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