

Acid Rain

READING: Chapter 13 of text;

- Gas-Liquid Partitioning and pH of "natural" rain
- US Acid Rain Problem: Sulfur and NO_x oxidation
- Trends in Emissions and Deposition

Guiding Questions:

What is acid rain?

What chemistry explains the low pH rain in the NE US?

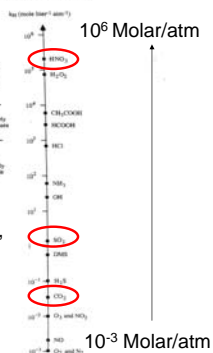
How do the natural sources of acidity compare to anthropogenic ones?

Henry's Law Constants

H_2SO_4 off scale

122

Cloud and precipitation chemistry



1 mole/liter of solution = 1 "Molar"

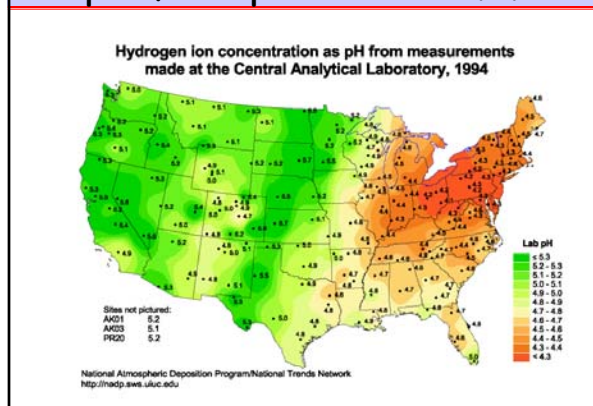
From Hobbs IAC

Question

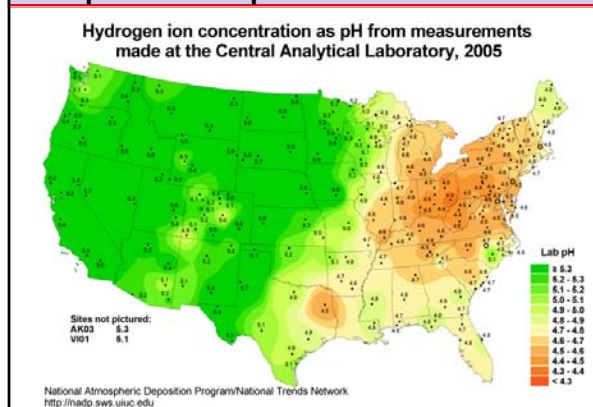
We saw that natural (preindustrial) rainwater was slightly acidic, pH ~ 5.7, just from the dissolution of $\text{CO}_{2(g)}$.

1. $\text{CO}_{2(g)}$ is expected to double later this century. If there were no other anthropogenic acids, by how much would the pH of natural rainwater change?

pH of Precipitation Over U.S.



pH of Precipitation Over U.S.

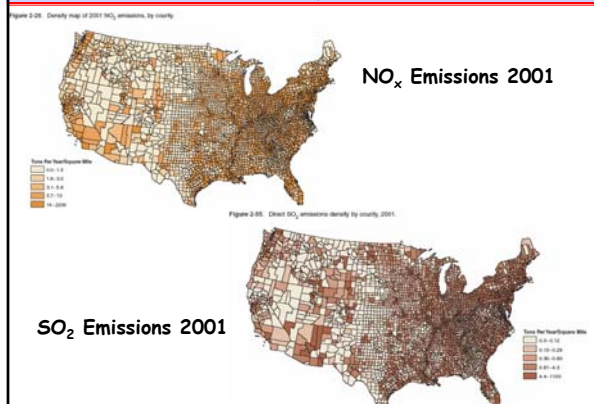


Chemical Composition of Precipitation

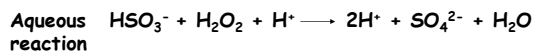
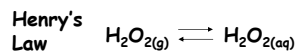
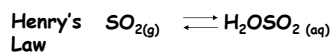
Table 13-1 Median Concentrations of Ions ($\mu\text{eq l}^{-1}$) in Precipitation at Two Typical Sites in the United States

Ion	Rural New York State	Southwest Minnesota
SO_4^{2-}	45	46
NO_3^-	25	24
Cl^-	4	4
HCO_3^-	0.1	10
Sum anions	74	84
H^+ (pH)	46 (4.34)	0.5 (6.31)
NH_4^+	8.3	38
Ca^{2+}	7	29
Mg^{2+}	1.9	6
K^+	0.4	2.0
Na^+	5	14
Sum cations	68	89

Patterns of U.S. NO_x and SO₂ Emissions

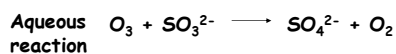
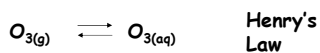
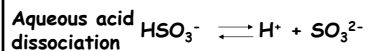
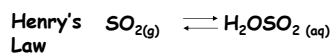


SO₂ Oxidation in Cloud by H₂O₂



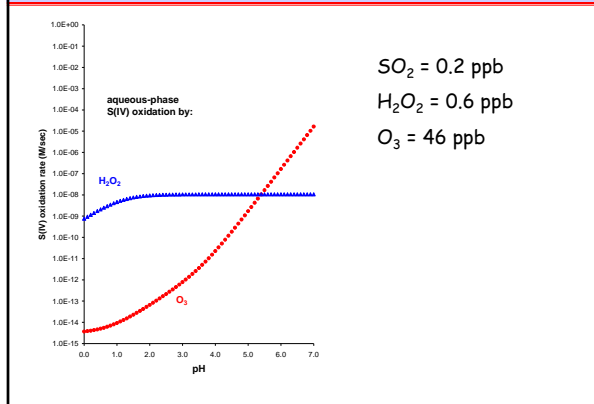
What happens in remote regions where H₂O₂ is low?

SO₂ Oxidation in Cloud by Ozone



Only important in remote regions or when cloud water pH > 6

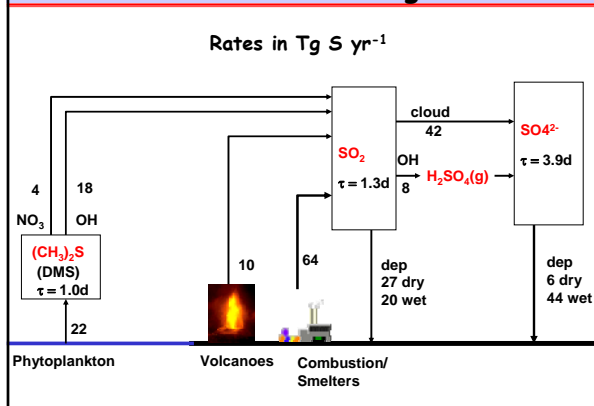
pH dependence of aqueous-phase SO_2 oxidation



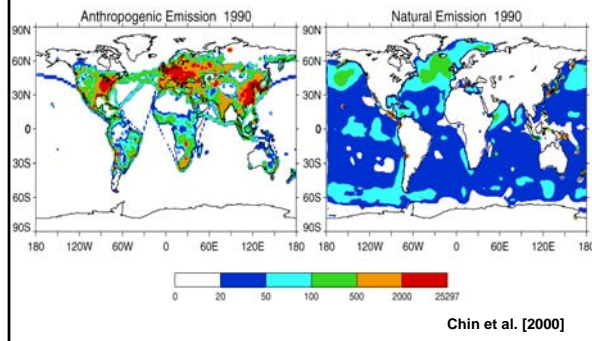
Question

1. How is it that the O_3 oxidation mechanism actually increases the acidity of precipitation?

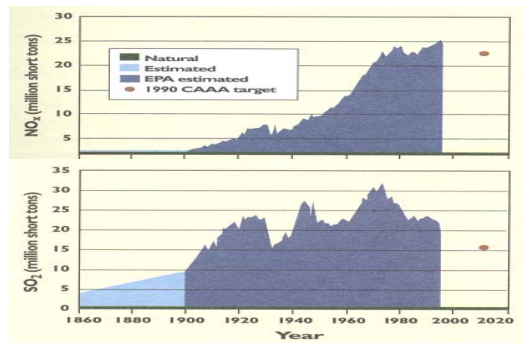
Global Sulfur Budget



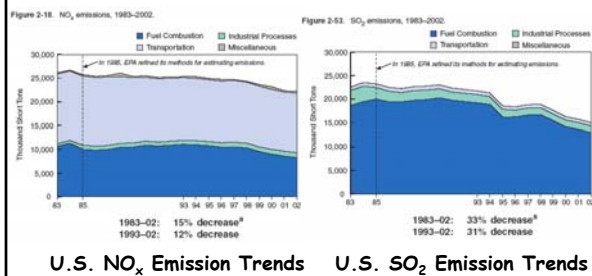
Global Sulfur Emission Patterns



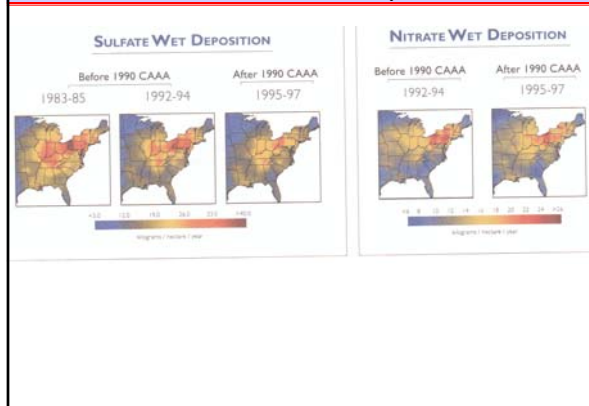
Trends in U.S. NO_x and SO₂ Emissions



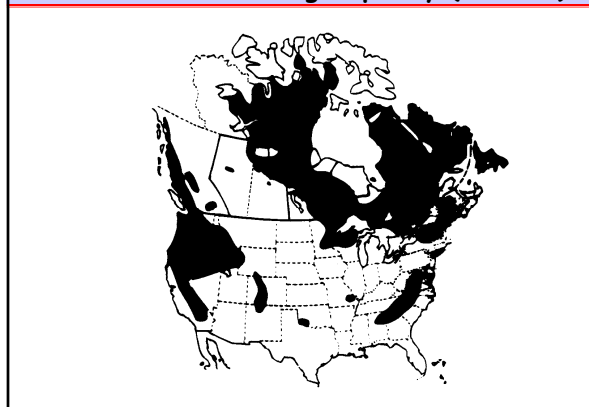
Trends in U.S. NO_x and SO₂ Emissions



Sulfate and Nitrate Wet Deposition Trends



Low Acid-Neutralizing Capacity (in black)

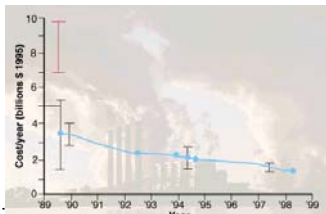


Cost-effectiveness of Acid Rain Program

- Costs = \$3 billion/year.
- Benefits = \$122 billion/year
[PM → human health; visibility; ecosystems]
- 40-to-1 benefit/cost ratio

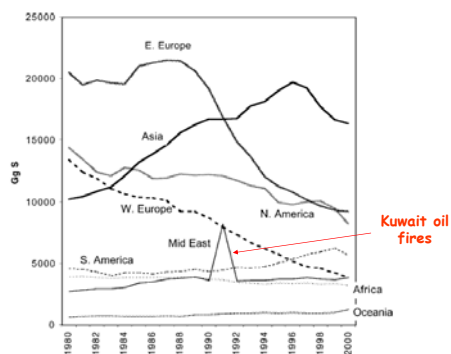
Costs of 1990 Clean air act amendment

- Initially estimated to be ~\$10 billion /year
- Actual costs ~\$1-2 billion/year
- cap and trade is more economical than strict regulations. Scrubbers turned out to be cheaper than expected and unexpected gains from switching to low sulfur coal



Kerr, Science, 1998.

Recent Trends in Sulfur Emissions (1980-2000)



Stern, Chemosphere 58 (2005)

Acid Rain Overview

Guiding Questions:

What is acid rain?

Precipitation (rain or fog) with a pH < ~ 5.5

What chemistry explains the low pH rain in the NE US?

Oxidation of Sulfur (SO_2) to H_2SO_4 primarily by in-cloud aqueous chemistry

Also, $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$

How do the natural sources of acidity compare to anthropogenic ones?

Anthropogenic sources of sulfur and NO_x currently dominate the natural sources

Presentation Guidelines/Tips

1. Aim for a 10 minute presentation (allowing 2 minutes for questions)
 - a. This isn't a whole lot of time—be judicious
2. Typical presentation contains:
 - a. *Title slide*
 - b. *Introduction*: define the problem and provide a "roadmap" or outline for your presentation
 - c. *Motivation*: answer "why should we listen?"
 - d. *Content*: What you did/learned and how does it relate to the course topics?
 - e. *Summary and Conclusions*: What would be next?

Presentation Guidelines/Tips

3. Try to make slides clear and concise
 - a. This is 24 pnt font - smaller than this becomes hard to read
 - b. 1 or 2 main points per slide
 - c. Less text is better—more diagrams and figures
4. Speak loudly and clearly
 - a. notecards are OK but try not to read from a script.

Presentation Guidelines/Tips

5. Practice your presentation!
6. I will take a quick look if you want
