Atmos. Chem. Lecture 16, 11/6/13: Acid formation in droplets

Acid rain

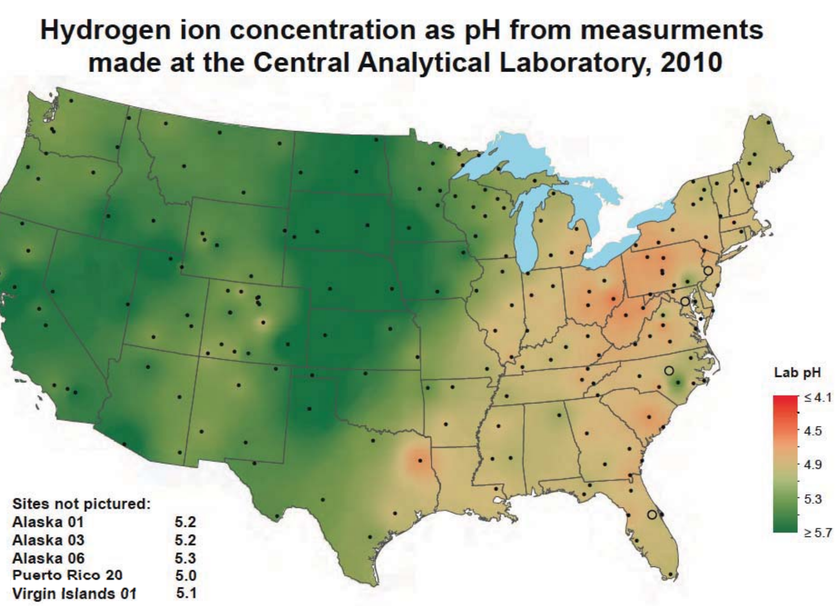
Review of S(IV) equilibria

Oxidation of S(IV) to S(VI)

Aqueous oxidation of other stuff

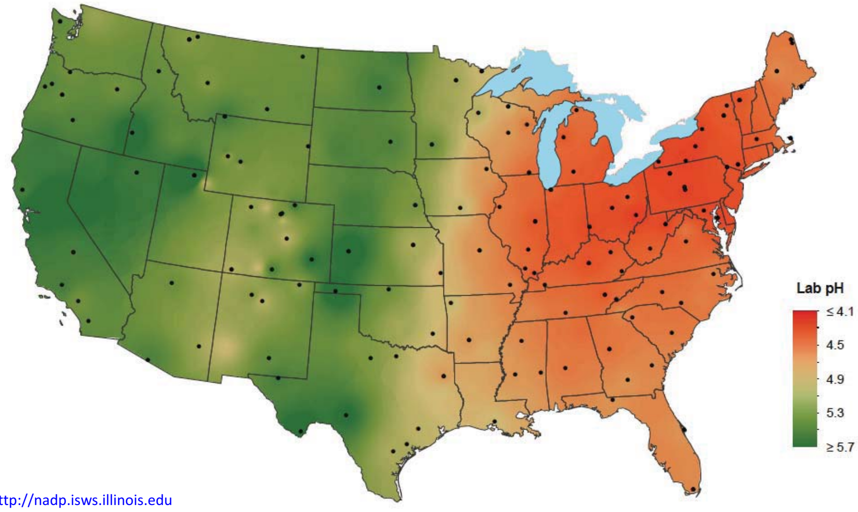
Proposals due Friday; PSet 4 due Mon Nov 25

Acid rain



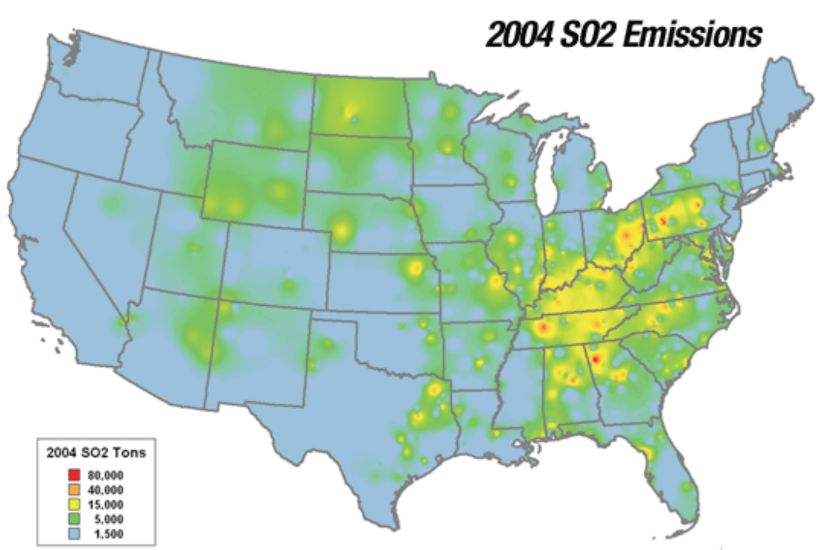
Acid rain

Hydrogen ion concentration as pH from measurments made at the Central Analytical Laboratory, 1985



http://nadp.isws.illinois.edu

Acid rain



Gas phase oxidation of NO_2, SO_2

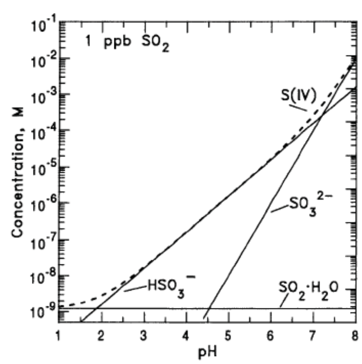
$NO_2 + OH \rightarrow HNO_3$

$SO_2 + OH \rightarrow HOSO_2$
$HOSO_2 + O_2 \rightarrow SO_3 + HO_2$
$SO_3 + H_2O \rightarrow H_2SO_4$

[Note: Additional material is discussed here during lecture.]

S(IV) aqueous equilibria

$SO_2(g) + H_2O \leftrightarrows SO_2 \bullet H_2O\ (aq)$
$SO_2 \bullet H_2O\ (aq) \leftrightarrows H^+ + HSO_3^-$
$HSO_3^- \leftrightarrows H^+ + SO_3^{2-}$



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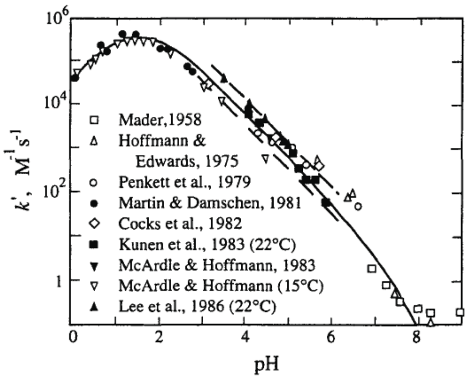
Oxidation of S(IV) to S(VI) by H_2O_2

$$H_2O_2 + HSO_3^- + H^+ \rightarrow SO_4^{2-} + 2H^+ + H_2O$$



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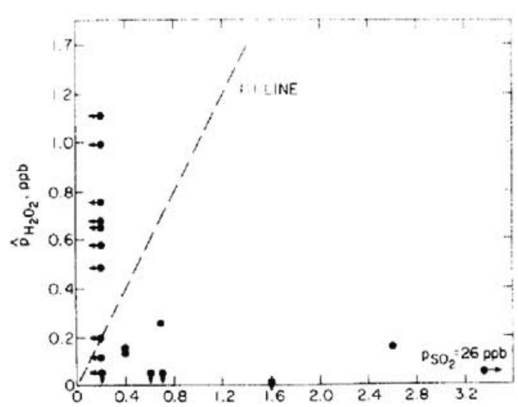
evidence for H_2O_2 + S(IV) reaction

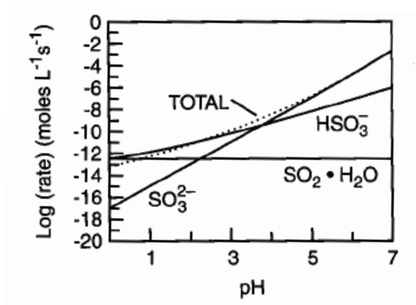


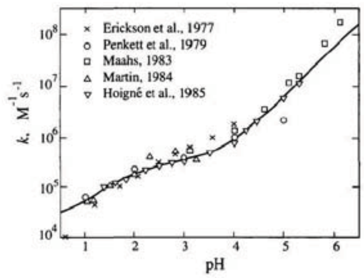
Daum et al., *Atmos. Environ.* 18:2671 (1984)

Oxidation of S(IV) to S(VI) by O_3

rapid reaction with S(IV) species

$$O_3 + SO_2{\cdot}H_2O \rightarrow H^+ + HSO_4^- + O_2$$
$$O_3 + HSO_3^- \rightarrow HSO_4^- + O_2$$
$$O_3 + SO_3^{2-} \rightarrow SO_4^{2-} + O_2$$





Oxidation of S(IV) to S(VI) by O_2

Medium	Manganese (μM)	Iron (μM)
Aerosol (haze)	0.1–100	100–1000
Clouds	0.01–10	0.1–100
Rain	0.01–1	0.01–10
Fog	0.1–10	1–100

Fe(III) catalysis

pH 0-3.6: $R = -\frac{d[S(IV)]}{dt} = k_{7.91}\frac{[Fe(III)][S(IV)]}{[H^+]}$

$$k_{7.91} = k^*_{7.91}\frac{10^{-2\sqrt{I}/(1+\sqrt{I})}}{1 + 150[S(VI)]^{2/3}}$$

pH 4.0 : $-\frac{d[S(IV)]}{dt} = 1 \times 10^9[S(IV)][Fe(III)]^2$

pH 5.0 to 6.0 : $-\frac{d[S(IV)]}{dt} = 1 \times 10^{-3}[S(IV)]$

pH 7.0 : $-\frac{d[S(IV)]}{dt} = 1 \times 10^{-4}[S(IV)]$

Mn(II) catalysis

high S(IV) concs:

$$-\frac{d[S(IV)]}{dt} = k_0[Mn]^2$$
$$k_0 = k_0^*\, 10^{-4.07\sqrt{I}/(1+\sqrt{I})}$$

low S(IV) concs:

$$-\frac{d[S(IV)]}{dt} = k_0[Mn][S(IV)]$$
$$k_0 = k_0^*\, 10^{-4.07\sqrt{I}/(1+\sqrt{I})}$$

Fe(III) + Mn(II) catalysis

rate = k_1[Mn(II)][S(IV)] + k_2[Fe(III)][S(IV)] + k3[Mn(II)][Fe(III)[S(IV)]

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Other metals as well (Ti, Cr., etc.): see Harris et al., *Science* 340:727 (2013)

Comparison of reaction rates

Images removed due to copyright restrictions. See Tables 7.19 and Figure 7.19 in Seinfeld, J. H., and S. H. Pandis. *Atmospheric Chemistry and Physics*, 2nd ed. Wiley 2006.

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Radical chemistry in cloud droplets

TABLE 8.9 Summary of Photochemistry of Some Species in Aqueous Solutions

Photochemical dissociation	Quantum yield[a]	Reference
$O_3 + h\nu(\lambda \leq 336\ nm) \xrightarrow{H_2O} H_2O_2$	$\Phi = 0.48$ at 254 nm 0.23 at 310 nm	Gurol and Akata, 1996 Taube, 1957
$H_2O_2 + h\nu(\lambda \leq 380\ nm) \rightarrow 2OH$	$\Phi^{OH}(308\ nm) = 0.98$ $\Phi^{OH}(351\ nm) = 0.96$ $\Phi^{OH}(250\ nm) = 1.8$	Zellner *et al.*, 1990; Zellner and Herrmann, 1995
$HONO + h\nu(\lambda \leq 390\ nm) \rightarrow OH + NO$	$\Phi^{OH}(280\text{–}390\ nm) = 0.35$	Fischer and Warneck, 1996
$HNO_3 + h\nu(\lambda \leq 320\ nm) \rightarrow OH + NO_2$	$\Phi = 0.1$[b]	Graedel and Weschler, 1981
$NO_2^- + h\nu(\lambda \leq 410\ nm) \xrightarrow{H_2O} NO + OH + OH^-$	$\Phi^{OH}(308\ nm) = 0.07$ $\Phi^{OH}(351\ nm) = 0.046$ $\Phi^{OH}(280\ nm) = 0.069$ $\Phi^{OH}(390\ nm) = 0.022$	Zellner *et al.*, 1990 Zellner *et al.*, 1990 Fischer and Warneck, 1996 Fischer and Warneck, 1996
$NO_3^- + h\nu(\lambda \leq 350\ nm) \rightarrow NO_2^- + O$ $\rightarrow NO_2 + O^- \xrightarrow{H_2O} OH^- + OH$	$\Phi^{O}(305\ nm) = 1.1 \times 10^{-3}$ $\Phi(305\text{–}313\ nm) = 0.013$	Warneck and Wurzinger, 1988; Zepp *et al.*, 1987; Zellner *et al.*, 1990; Zellner and Herrmann, 1995
$HO_2^- + h\nu(\lambda \leq 390\ nm) \xrightarrow{H_2O} OH + OH^- + O_2$		Treinin, 1970

[a] These are *effective quantum yields*, that is, those for photolysis and escape of the species from the solvent cage.
[b] Estimated.

also halogen reactions, Fe(II)-Fe(III) chemistry…

Oxidation of S(IV) by OH (aq)

$$OH + HSO_3^- \rightarrow H_2O + SO_3^-$$
$$OH + SO_3^{-2} \rightarrow OH^- + SO_3^-$$

$$SO_3^- + O_2 \rightarrow SO_5^-$$
$$SO_5^- + HSO_3^- \rightarrow HSO_4^- + SO_4^-$$
$$SO_5^- + HSO_3^- \rightarrow HSO_5^- + SO_3^-$$
$$HSO_5^- + HSO_3^- + H^+ \rightarrow 2SO_4^{-2} + 3H^+$$
$$SO_5^- + SO_3^{-2} \rightarrow SO_4^- + SO_4^-$$
$$SO_4^- + HSO_3^- \rightarrow HSO_4^- + SO_3^-$$
$$SO_4^- + SO_3^{-2} \rightarrow SO_4^{-2} + SO_3^-$$
$$SO_4^- + H_2O \rightarrow HSO_4^- + OH$$
$$SO_5^- + SO_5^- \rightarrow 2SO_4^- + O_2$$

$$SO_5^- + SO_5^- \rightarrow S_2O_8^{-2} + O_2$$
$$SO_4^- + SO_4^- \rightarrow S_2O_8^{-2}$$

New gas-phase S(IV) oxidation pathway

Science 335:204 (2012)
[alsp *Science* 340:177 (2013)]

Aqueous oxidation of other species: NO_x

H_{HNO3} = 2.1x10^5 M/atm
H_{NO} = 1.9x10^{-3} M/atm
H_{NO2}=1.0x10^{-2} M/atm

But: nitrite, nitrate has important aqueous chemistry

[Note: Additional material is discussed here during lecture.]

Aqueous oxidation of other species: Organics

$CH_2O(g) \leftrightarrows CH_2O(aq)$
$CH_2O(aq) + H_2O \leftrightarrows CH_2(OH)_2$

$CH_2(OH)_2 + OH + O_2 \rightarrow HCOOH$ *forms acid!*
$HCOOH \leftrightarrows H^+ + HCOO^-(aq)$

[Note: Additional material is discussed here during lecture.]

1.84J / 10.817J / 12.807J Atmospheric Chemistry
Fall 2013