Irreversible Aqueous Chemistry

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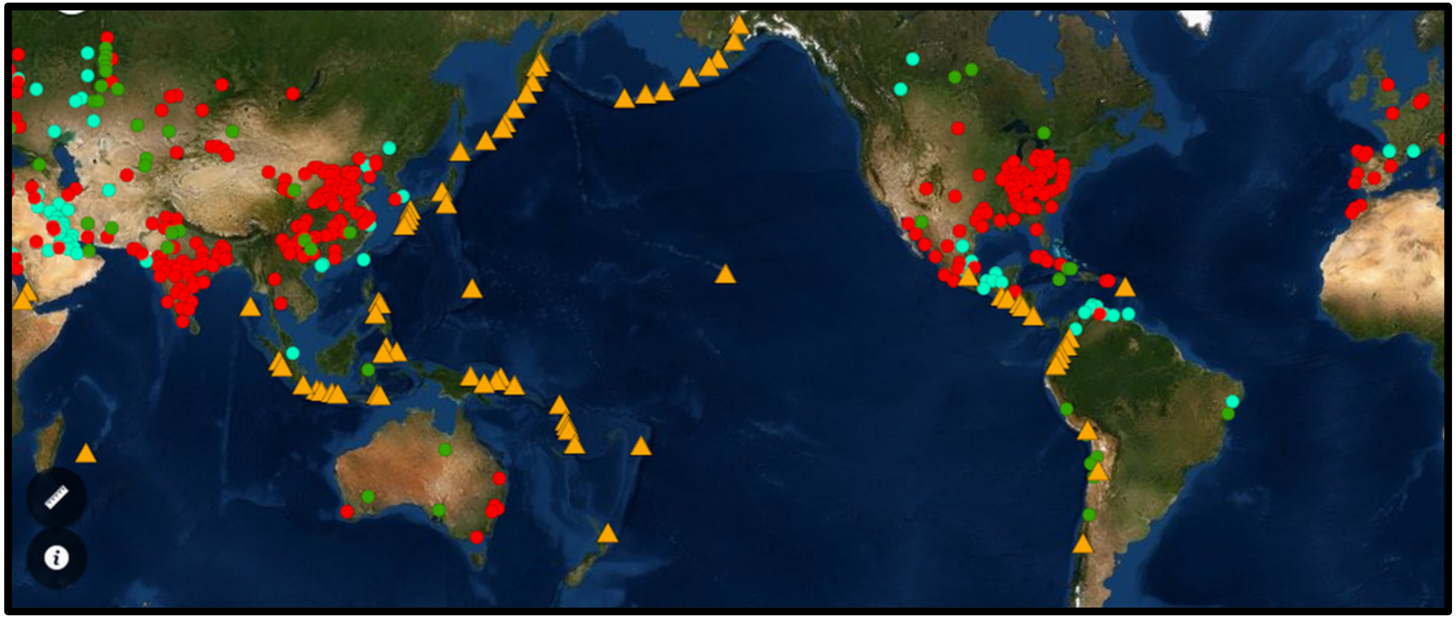
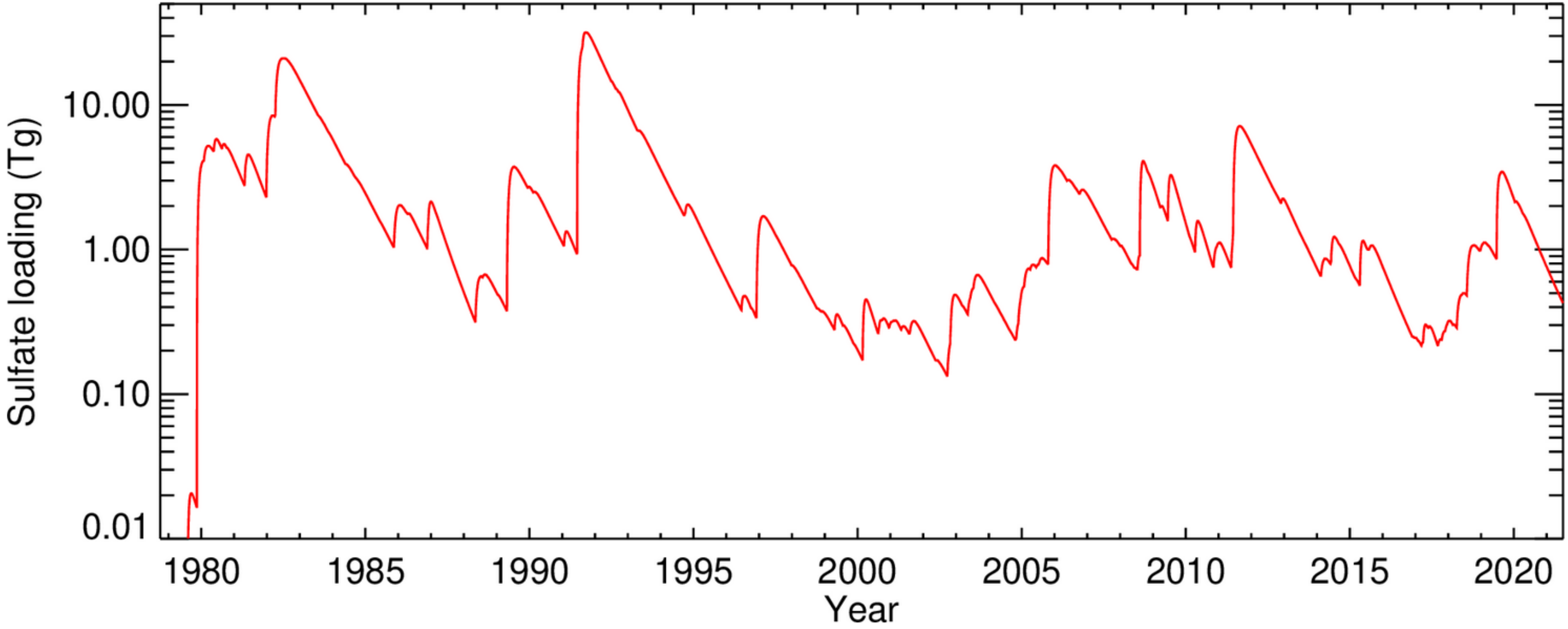
Chapter 19 - Fundamentals of Atmospheric Modeling

OMI Annual SO2 Emissions Summary by Country
https://so2.gsfc.nasa.gov/measures.html



CYAN means Oil and Gas, RED means Power Plant, GREEN means Smelter, and ORANGE is a Volcano.

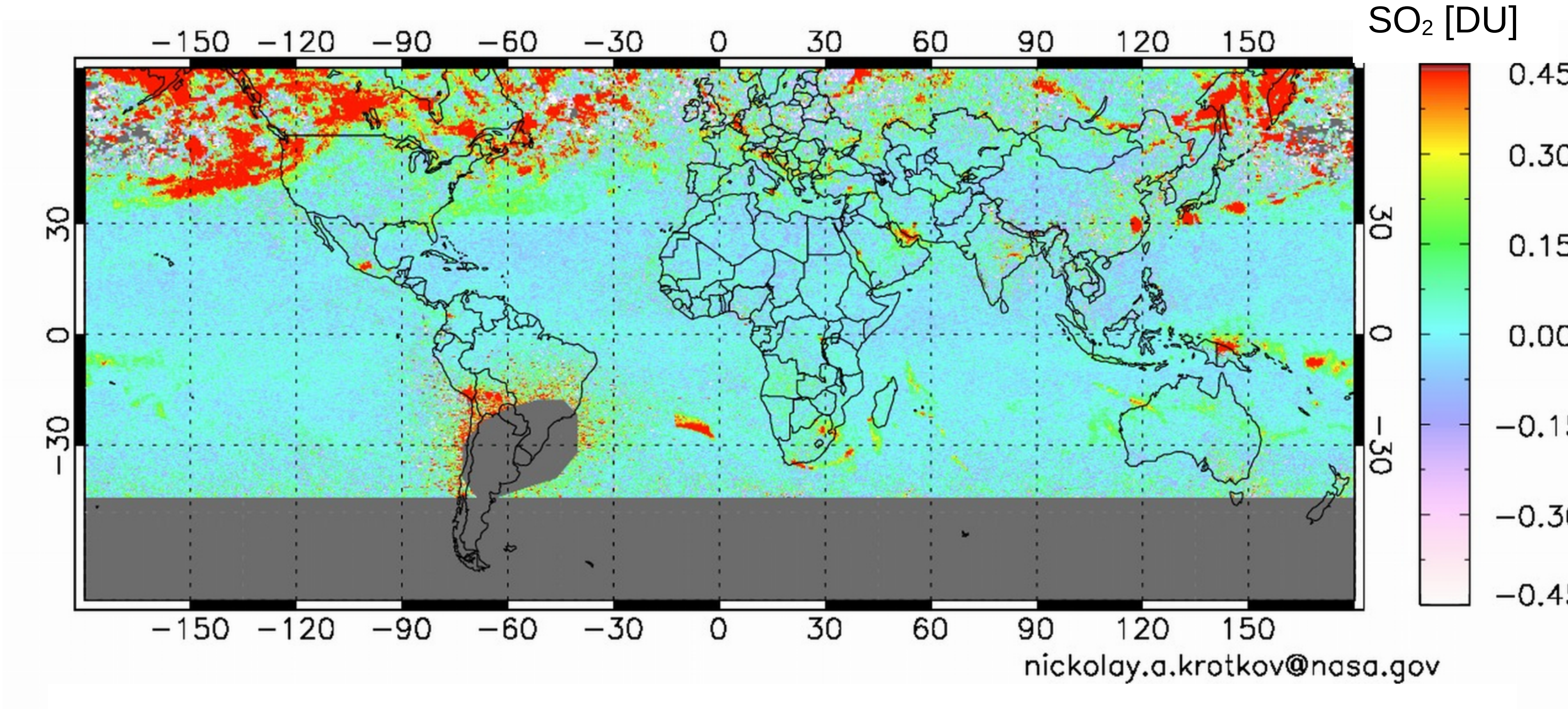
Stratospheric Sulfate Loading (Tg)



The SO_2 mass for all significant explosive eruptions in our database (VEI 3+) was converted to sulfate mass in this plot using a typical SO2/sulfate mass ratio (assuming complete conversion of SO_2 to sultate aerosol with composition 75 wt% H_2SO_4 - 25 wt% H_2O). To simulate the decay of sulfate aerosol mass with time we assumed a fixed, latitude-dependent e-folding time.

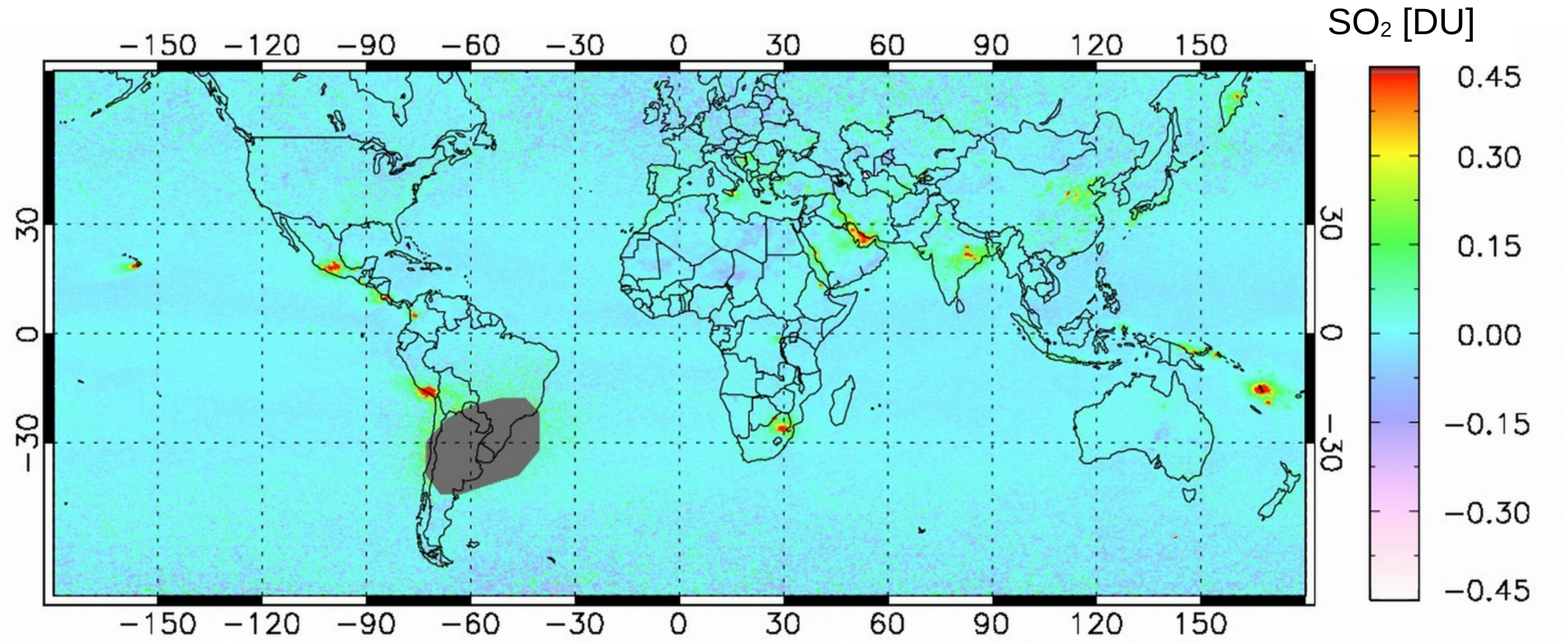
https://so2.gsfc.nasa.gov/measures.html

2019/07 Monthly Mean Aura/OMI PBL SO_2



https://gs614-avdc1-pz.gsfc.nasa.gov/pub/data/satellite/Aura/OMI/V03/L3/OMSO2m/

2017 Yearly Mean Aura/OMI PBL SO_2

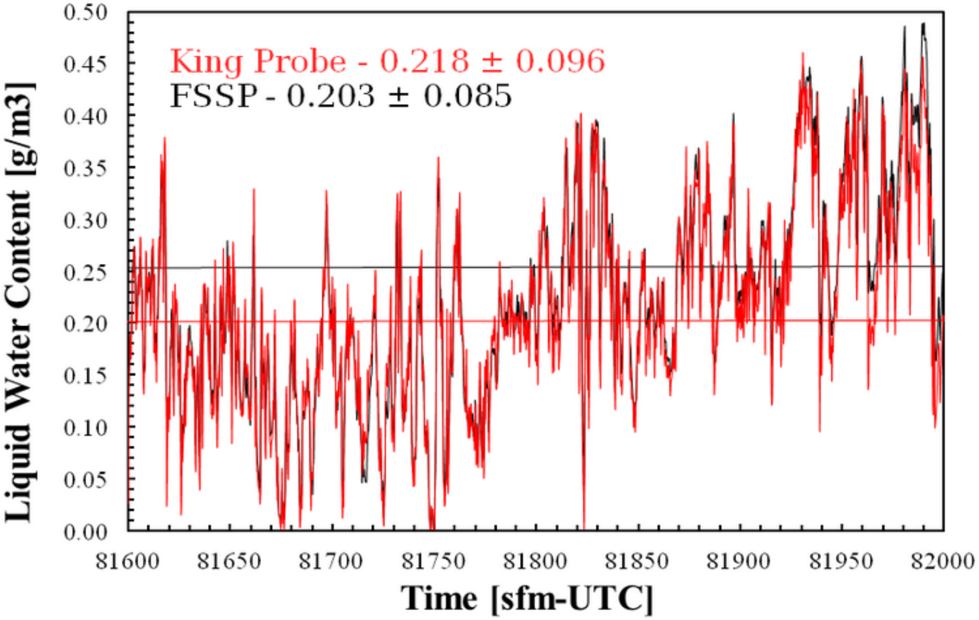


https://gs614-avdc1-pz.gsfc.nasa.gov/pub/data/satellite/Aura/OMI/V03/L3/OMSO2m/

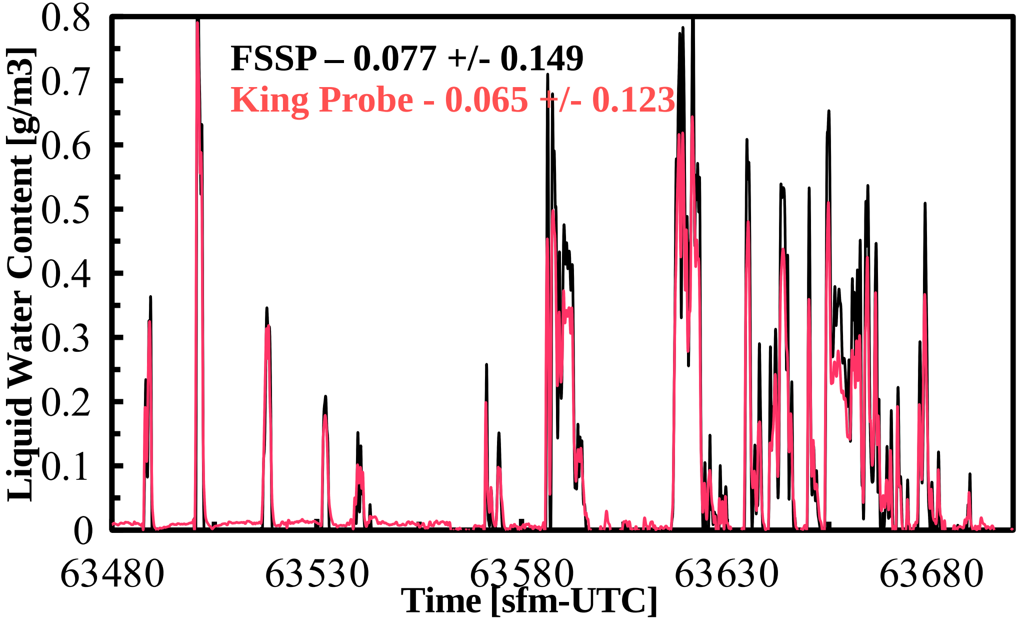
Gas Dissolution ~ Liquid Water Quality

Aqueous chemistry proceeds faster in cloud drops, which generally have liquid-water contents $>10^5$ µg m^{-3} , than in aerosol particles, which have liquid-water contents <500 µg m^{-3} .

March 10, 2004 Citation Flight

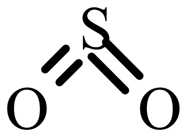


September 24, 2004 Citation Flight

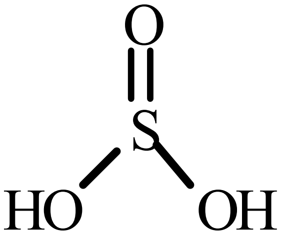


S(IV) Family (+4 Oxidation State)

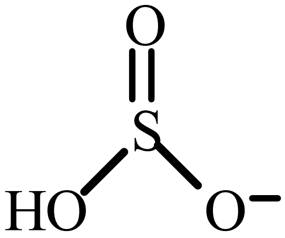
Sulfur Dioxide
SO_2(g,aq)



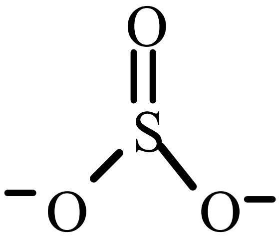
Sulfurous Acid
H_2SO_3(aq)



Bisulfite Ion
HSO_3^-

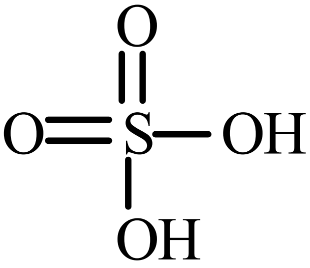


Sulfite Ion
SO_3^{2-}

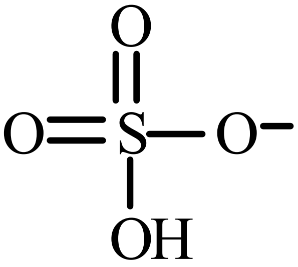


S(VI) Family (+6 Oxidation State)

Sulfuric Acid
H_2SO_4(g,aq)



Bisulfate Ion
HSO_4^-



Sulfate Ion
SO_4^{2-}

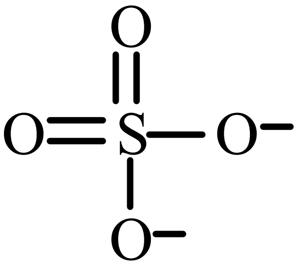


Table 19.1

Henry’s Law – Gas Dissolution

- Over a dilute solution, the pressure exerted by a gas is proportional to the molality of the dissolved gas in solution (Section 17.4).

- The quantity of gas over a drop surface is the saturation vapor pressure of the gas, and the gas is in equilibrium with its dissolved phase at the surface.

- In the absence of aqueous chemistry, only a finite amount of a gas dissolves in a liquid drop.

- When irreversible chemistry occurs, the dissolved gas chemically reacts to produce a product, instantaneously decreasing the molality of the dissolved gas and more gas must dissolve into the drop to maintain saturation.

Mechanisms of Converting S(IV) to S(VI)

Why is converting S(IV) to S(VI) important?

It allows sulfuric acid to enter or form within cloud drops and aerosol particles, increasing their acidity. Sulfuric Acid is main source of acidity in rain water.

Mechanisms (Convert Sulfur Dioxide Gas to Dissolved Sulfuric Acid)

1. Gas-phase oxidation of $SO_2(g)$ to $H_2SO_4(g)$ followed by condensation of $H_2SO_4(g)$.
2. Dissolution of $SO_2(g)$ into liquid water to form $H_2SO_3(aq)$ followed by aqueous chemical conversion of $H_2SO_3(aq)$ and its dissociation products to $H_2SO_4(aq)$ and its dissociation products.

Bisulfate and Sulfate are Dissociation products of Sulfuric Acid

Gas-Phase Oxidation of S(IV)

(1) Gas-phase Oxidation of Sulfur Dioxide to Sulfuric Acid

$$SO_2(g) \xrightarrow{+\dot{O}H(g),\ M} HS\dot{O}_3(g) \xrightarrow[\dot{H}O_2(g)]{+O_2(g)} SO_3(g) \xrightarrow{+H_2O(g)} H_2SO_4(g) \qquad (19.1)$$

$SO_2(g)$	$HS\dot{O}_3(g)$	$SO_3(g)$	$H_2SO_4(g)$
Sulfur dioxide gas	Bisulfite	Sulfur trioxide	Sulfuric acid gas

Condenses → Irreversible

(2) Condensation and Dissociation of Sulfuric Acid

$$H_2SO_4(g) \longrightarrow H_2SO_4(aq) \rightleftharpoons H^+ + HSO_4^- \rightleftharpoons 2H^+ + SO_4^{2-} \qquad (19.2)$$

$H_2SO_4(g)$	$H_2SO_4(aq)$	$H^+ + HSO_4^-$	$2H^+ + SO_4^{2-}$
Sulfuric acid gas	Aqueous sulfuric acid	Bisulfate ion	Sulfate ion

Dissociation of sulfuric acid releases two protons, decreasing pH and increasing acidity.

S(IV) Dissolution/Aqueous Oxidation

(1) Dissolution of Sulfur Dioxide

$$\underset{\text{Sulfur dioxide gas}}{SO_2(g)} \rightleftharpoons \underset{\text{Dissolved sulfur dioxide}}{SO_2(aq)} \qquad (19.3)$$

Volume-limited Process

(2) Dissociation of Dissolved Sulfur Dioxide

At pH of 2-7, most S(IV) dissociates to HSO_3^-

$$\underset{\text{Dissolved sulfur dioxide}}{SO_2(aq)} + \underset{\text{Liquid water}}{H_2O(aq)} \rightleftharpoons \underset{\text{Sulfurous acid}}{H_2SO_3(aq)} \rightleftharpoons \underset{\text{Hydrogen ion}}{H^+} + \underset{\text{Bisulfite ion}}{HSO_3^-} \rightleftharpoons \underset{\text{Hydrogen ion}}{2H^+} + \underset{\text{Sulfite ion}}{SO_3^{2-}} \qquad (19.4)$$

Aqueous Oxidation of S(IV)

(3) Oxidation of S(IV) by Hydrogen Peroxide (H_2O_2)

$$HSO_3^- + H_2O_2(aq) + H^+ \longrightarrow SO_4^{2-} + H_2O(aq) + 2H^+ \qquad (19.5)$$

Bisulfite ion Hydrogen peroxide (aq) Sulfate ion

Lower pH (aerosols) have higher rate coefficients; however, aerosols contain less H_2O_2(aq) and liquid water, therefore less efficient reaction than cloud drops.

If $[H_2O_2(aq)] > [S(IV)]$

S(IV) is consumed within tens of minutes.

If $[S(IV)] > [H_2O_2(aq)]$

H_2O_2(aq) is consumed within minutes.

Hydrogen Peroxide Sources/Sinks

Sinks of Hydrogen Peroxide in Liquid Water

Photolyzed

$$H_2O_2(aq) + h\nu \longrightarrow 2\dot{O}H(aq) \qquad (19.6)$$

$$H_2O_2(aq) + \dot{O}H(aq) \longrightarrow H_2O(aq) + H\dot{O}_2(aq) \qquad (19.7)$$

Sources of Hydrogen Peroxide in Liquid water

$$H_2O_2(g) \rightleftharpoons H_2O_2(aq) \qquad (19.8)$$

$$\underset{\text{Hydroperoxy radical}}{H\dot{O}_2(aq)} + \underset{\text{Peroxy ion}}{O_2^-} + H_2O(aq) \longrightarrow \underset{\text{Hydrogen peroxide}}{H_2O_2(aq)} + O_2(aq) + \underset{\text{Hydroxide ion}}{OH^-} \qquad (19.9)$$

Aqueous Oxidation of S(IV)

Oxidation by Dissolved Ozone

Important when pH > 6 (Only Cloud Drops with ammonium and sodium)

Most Important Reaction

$$SO_3^{2-} + O_3(aq) \longrightarrow SO_4^{2-} + O_2(aq) \qquad (19.11)$$

Sulfite ion — Dissolved ozone — Sulfate ion — Dissolved oxygen

What does 19.11 do to gas phase ozone?

Oxidation by Hydroxyl Radical

Important when liquid-water content exceeds 0.2 g m^{-3} and pH ≈ 5

$$HSO_3^- + \dot{O}H(aq) + O_2(aq) \longrightarrow S\dot{O}_5^- + H_2O(aq) \qquad (19.12)$$

Bisulfite ion — Peroxysulfate ion

Aqueous Oxidation of S(IV)

(1) Oxidation by Dissolved Oxygen: Catalyzed by Peroxysulfate Ion (SO_5-)

$$\underset{\substack{\text{Bisulfite}\\ \text{ion}}}{HSO_3^-} + \underset{\substack{\text{Dissolved}\\ \text{oxygen}}}{O_2(aq)} \xrightarrow{S\dot{O}_5^-} \underset{\substack{\text{Peroxymonosulfate}\\ \text{ion}}}{HSO_5^-} \qquad (19.13)$$

(2) Oxidation by the Peroxymonosulfate Ion

$$\underset{\substack{\text{Bisulfite}\\ \text{ion}}}{HSO_3^-} + HSO_5^- + H^+ \longrightarrow \underset{\substack{\text{Sulfate}\\ \text{ion}}}{2SO_4^{2-}} + 3H^+ \qquad (19.14)$$

Aqueous Oxidation of S(IV)

Oxidation by Dissolved Oxygen: Catalyzed by Fe(III)=Fe^{3+}

$$\mathrm{SO_3^{2-} + H_2O(aq) + O_2(aq) \xrightarrow{Fe(III)} SO_4^{2-} + H_2O_2(aq)} \qquad (19.15)$$

Sulfite ion

Sulfate ion

Oxidation by Dissolved Oxygen: Catalyzed by Mn(II) = Mn^{2+}

$$\mathrm{HSO_3^{-} + H_2O(aq) + O_2(aq) \xrightarrow{Mn(II)} SO_4^{2-} + H_2O_2(aq) + H^{+}} \qquad (19.16)$$

Bisulfite ion

Sulfate ion

Aqueous Oxidation of S(IV)

Formaldehyde (produced by combustion and photochemistry) Equilibrates with Methylene Glycol

$$HCHO(aq) + H_2O(aq) \rightleftharpoons H_2C(OH)_2(aq) \tag{19.17}$$

Formaldehyde

Methylene glycol

Oxidation by Formaldehyde (HCHO) at High pH

$$SO_3^{2-} + HCHO(aq) \longrightarrow HOCH_2SO_3^{-} + OH^{-} \tag{19.19}$$

Sulfite ion

Formaldehyde

HMSA
(Hydroxymethanesulfonate)

Aqueous Oxidation of S(IV)

Dichloride Ion Equilibrates with Chlorine Atom, Ion

$$\underset{\text{Dichloride ion}}{Cl_2^-} \rightleftharpoons \underset{\text{Chlorine atom}}{\dot{C}l(aq)} + \underset{\text{Chloride ion}}{Cl^-} \qquad (19.21)$$

What is a source for Chlorine Atom?

Oxidation by Dichloride Ion

$$\underset{\text{Bisulfite ion}}{HSO_3^-} + \underset{\text{Dichloride ion}}{Cl_2^-} + O_2(aq) \longrightarrow \underset{\text{Peroxysulfate ion}}{S\dot{O}_5^-} + 2Cl^- + H^+ \qquad (19.24)$$

Summarizing, what does the conversion rate of S(IV) to S(VI) depend on?

Change in S(VI) content when SO_2(g) dissolved and did not react (a) and did react (b) in a cloud. H2SO4 condensed in both cases, but So2 dissolved and reacted in the second case only. The conversion took < 10 minutes.

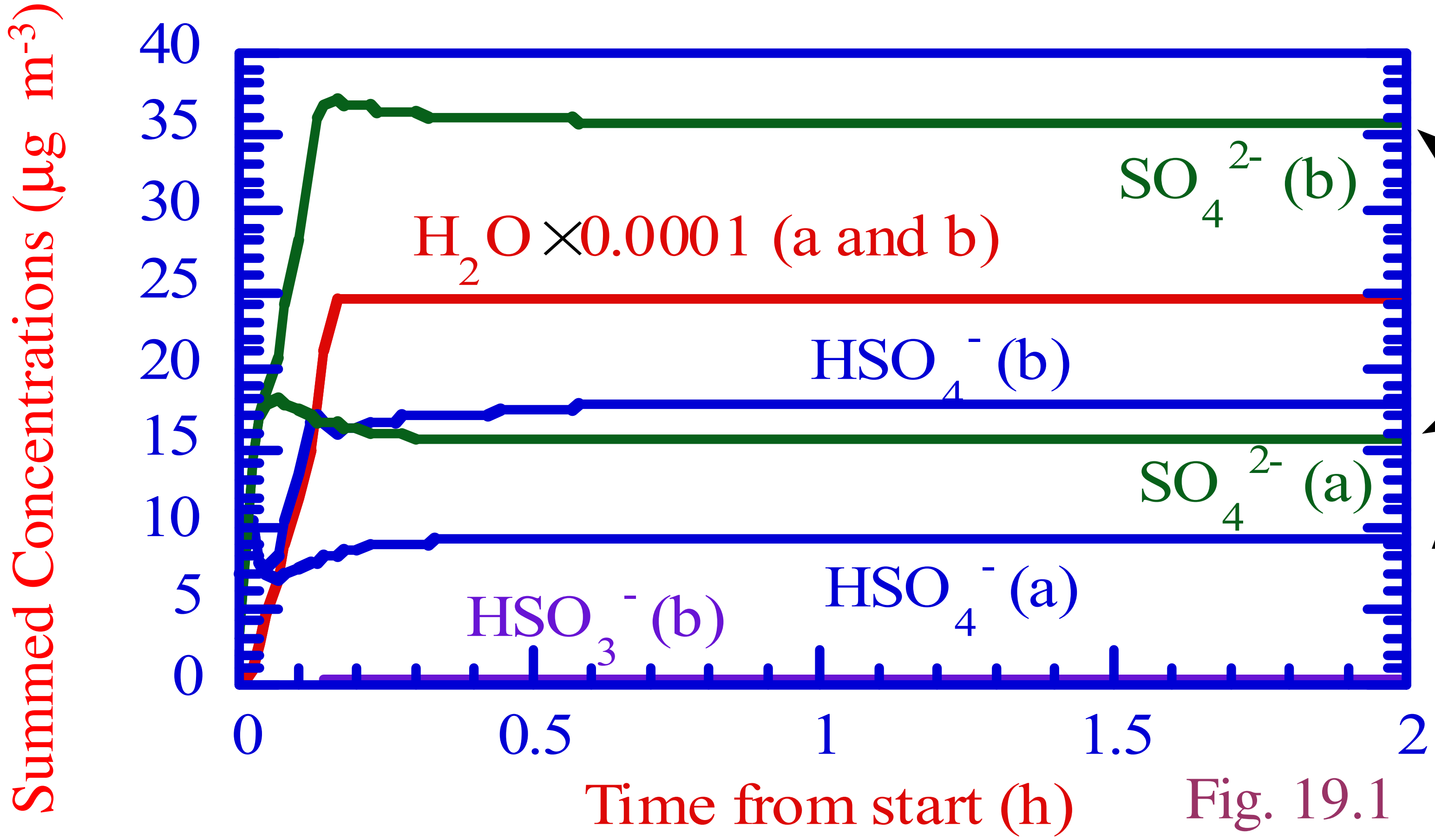


Fig. 19.1

Important of Clouds

Aerosols require hours to days.

PH Level of Selected Solutions

What cause the pH of rain and fog to be in rnage of 2-5.6?

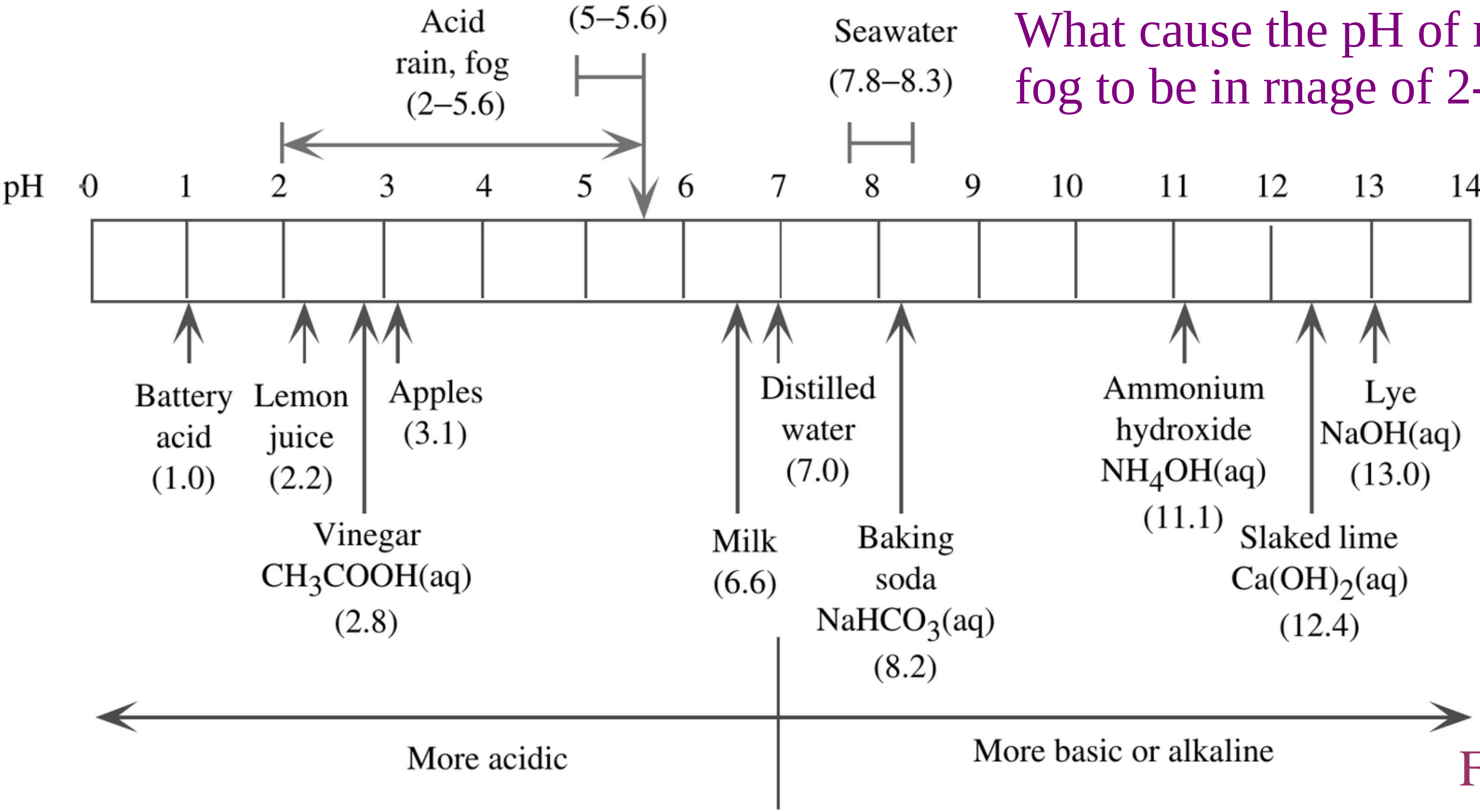
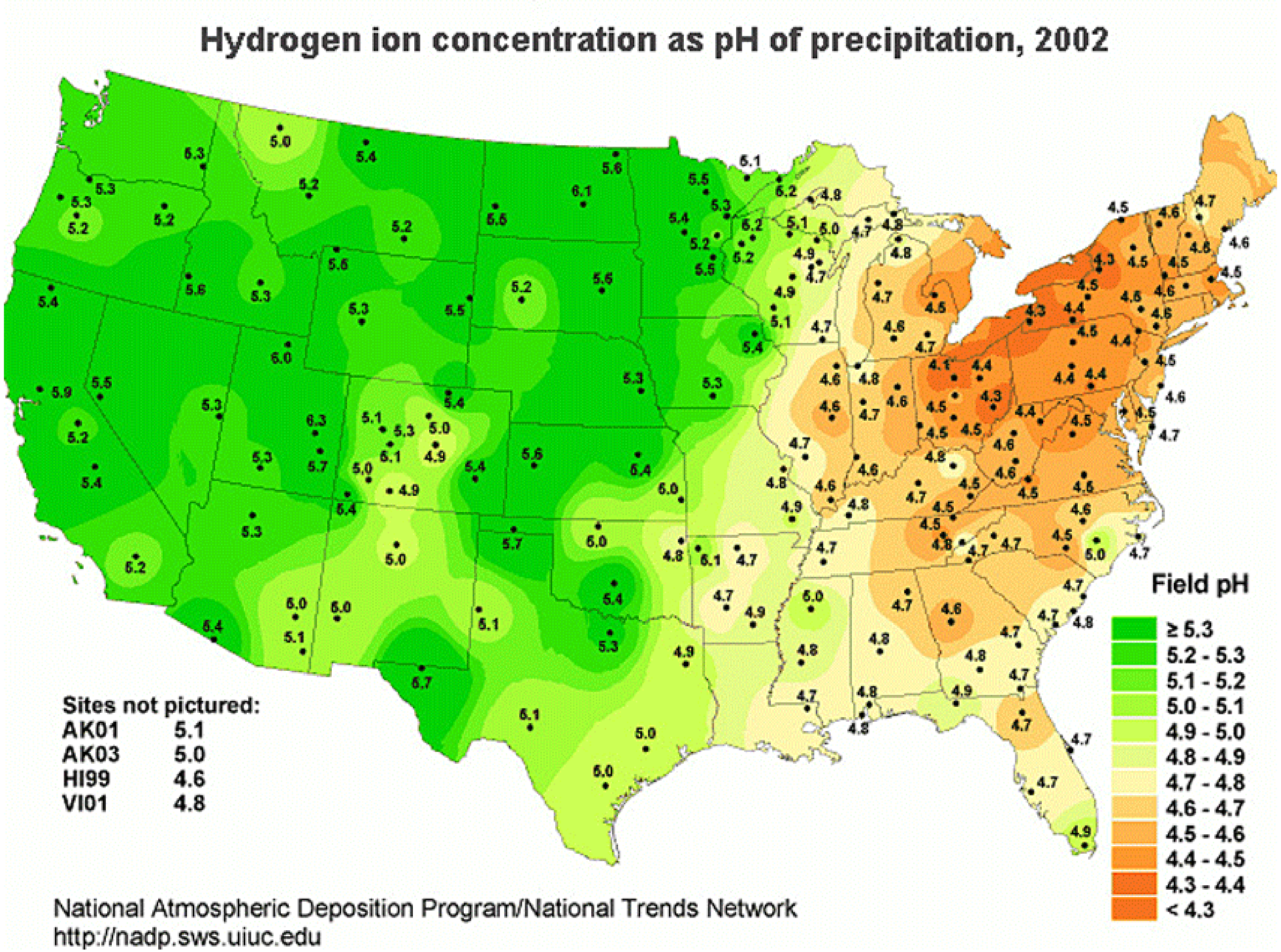


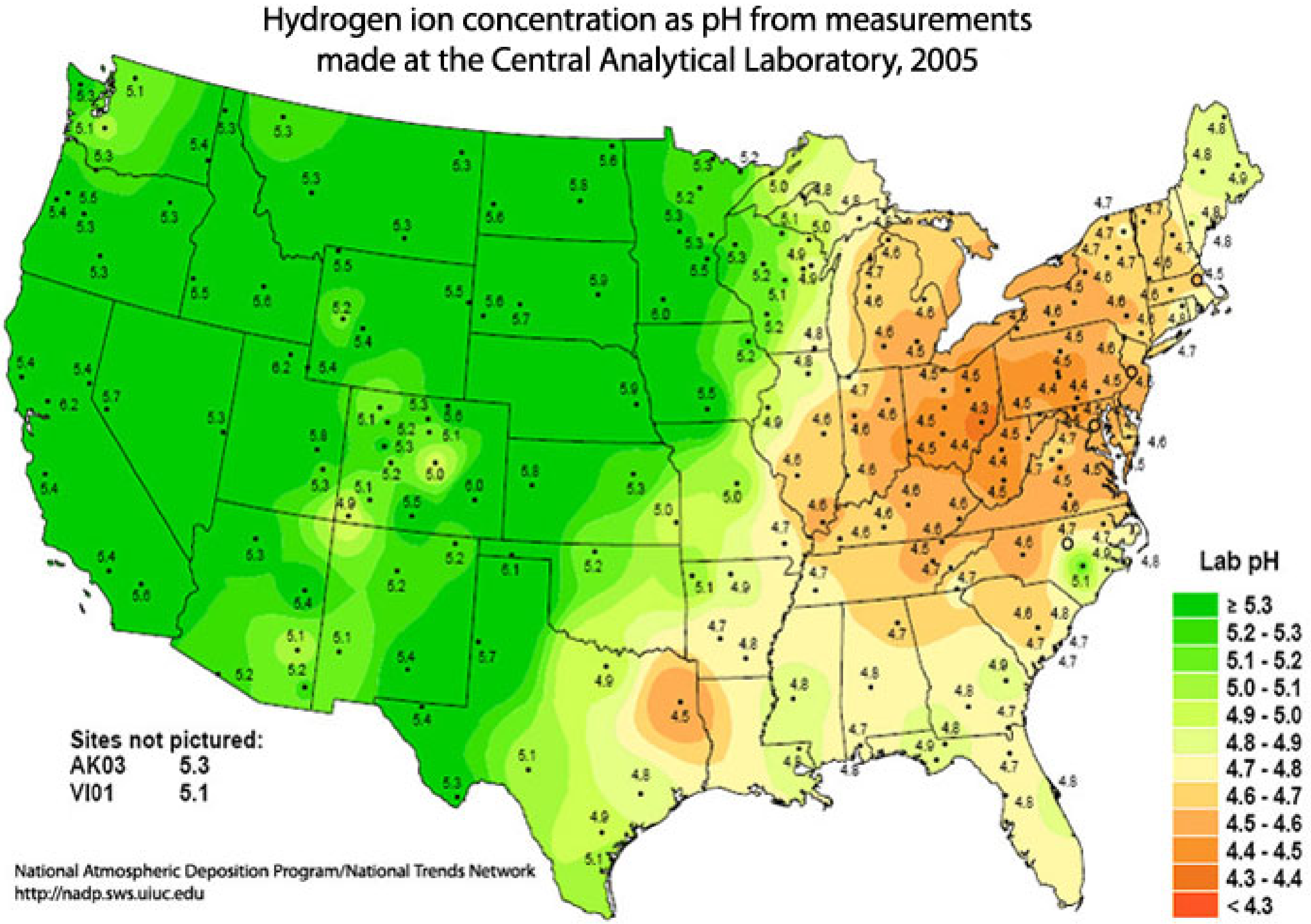
Fig. 17.1

Precipitation pH



https://www.usgs.gov/media/images/ph-rainfall-usa-2002

Precipitation pH



Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2005

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

https://www.learner.org/courses/envsci/visual/visual.php?shortname=hydrogen_ion

19.3 Diffusion Within a Drop

Characteristic time (τ) for aqueous diffusion in cloud drop.

$$\tau_{ad,q} = \frac{r_i^2}{\pi^2 D_{aq,q}} \qquad (19.25)$$

r_i – Radius of Drop

$D_{aq,q}$ – Diffusion Coefficient

Example 19.1: From Equation 19.25

$d_i = 30$ μm ---> $\tau_{ad,q} = 0.011$ s

$d_i = 10$ μm ---> $\tau_{ad,q} = 0.0013$ s

Reaction times for O_3(aq), NO_3(aq), OH(aq), Cl(aq), SO_4^- CO_3^-, and Cl_2^- are shorter than are diffusion transport times.

Diffusion Within a Drop

Time rate of change of concentration of species *q* in size bin *i* as a function of radius during diffusion

$$\left(\frac{\mathrm{d}c_{q,i,r}}{\mathrm{d}t}\right)_{ad,aq} = D_{aq,q}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_{q,i,r}}{\partial r}\right) + P_{c,q,i,r} - L_{c,q,i,r} \qquad (19.26)$$

Boundary Condition

At drop center, $\partial c_{q,i,r} / \partial r = 0$

19.4 Aqueous Chemistry With Growth

Aqueous reactions stiffer than gas reactions

Aqueous reactions solved in more size bins than gas reactions

Aqueous concentrations coupled to growth and equilibrium

--> Either time split aqueous chemistry from other processes with a small splitting time step or solve aqueous chemistry together with other processes

Change in Aerosol Composition

$$\left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{ge,eq,aq} = \left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{ge} + \left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{eq} + \left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{aq} \qquad (19.27)$$

Corresponding conservation of gas equation

$$\frac{\mathrm{d}C_{q,t}}{\mathrm{d}t} = -\sum_{i=1}^{N_B}\left(\frac{\mathrm{d}c_{q,i,t}}{\mathrm{d}t}\right)_{ge} \qquad (19.28)$$

Aqueous Chemistry Families

Used for one type of numerical solution to aqueous chemistry

$$c_{\mathrm{S(IV)},i} = c_{\mathrm{SO_2(aq)},i} + c_{\mathrm{HSO_3^-},i} + c_{\mathrm{SO_3^{2-}},i}$$

$$c_{\mathrm{S(VI)},i} = c_{\mathrm{H_2SO_4(aq)},i} + c_{\mathrm{HSO_4^-},i} + c_{\mathrm{SO_4^{2-}},i}$$

$$c_{\mathrm{HO}_{2,T},i} = c_{\mathrm{HO_2(aq)},i} + c_{\mathrm{O_2^-},i}$$

$$c_{\mathrm{CO}_{2,T},i} = c_{\mathrm{CO_2(aq)},i} + c_{\mathrm{HCO_3^-},i} + c_{\mathrm{CO_3^{2-}},i}$$

$$c_{\mathrm{HCHO}_T,i} = c_{\mathrm{HCHO(aq)},i} + c_{\mathrm{H_2C(OH)_2},i}$$

$$c_{\mathrm{HCOOH}_T,i} = c_{\mathrm{HCOOH(aq)},i} + c_{\mathrm{HCOO^-},i}$$

$$c_{\mathrm{CH_3COOH}_T,i} = c_{\mathrm{CH_3COOH(aq)},i} + c_{\mathrm{CH_3COO^-},i}$$

(19.29)-(19.35)

Growth/Aqueous Chemistry ODEs

Change in S(IV) due to aqueous chemistry (19.43)

$$\frac{\mathrm{d}c_{\mathrm{S(IV)},i,t}}{\mathrm{d}t} = k_{\mathrm{S(IV)},i,t-h}\left(C_{\mathrm{SO_2(g)},t} - S'_{\mathrm{S(IV)},i,t-h}\frac{c_{\mathrm{S(IV)},i,t}}{H'_{\mathrm{S(IV)},i,t-h}} \right) + P_{c,\mathrm{S(IV)},i,t} - L_{c,\mathrm{S(IV)},i,t}$$

Chemical production and loss terms (19.45)

$$P_{c,q,i,t} = \sum_{l=1}^{N_{prod,q}} R_{c,n_P(l,q),t} \qquad L_{c,q,i,t} = \sum_{l=1}^{N_{loss,q}} R_{c,n_L(l,q),t}$$

Gas conservation equation (19.53)

$$\frac{\mathrm{d}C_{\mathrm{SO_2(g)},t}}{\mathrm{d}t} = -\sum_{i=1}^{N_B} k_{\mathrm{S(IV)},i,t-h}\left[C_{\mathrm{SO_2(g)},t} - S'_{\mathrm{S(IV)},i,t-h}\frac{c_{\mathrm{S(IV)},i,t}}{H'_{\mathrm{S(IV)},i,t-h}} \right]$$

Growth/Aqueous Chemistry ODEs

Dimensionless effective Henry's constant (19.44)

$$H'_{\mathrm{S(IV)},i,t-h} = H'_{\mathrm{SO_2(aq)},i} \frac{c_{\mathrm{S(IV)},i,t}}{c_{\mathrm{SO_2(aq)},i,t}}$$

$$= m_v c_{w,i,t-h} R^* T H_{\mathrm{SO_2}} \left(1 + \frac{K_{1,\mathrm{S(IV)}}}{\mathbf{m}_{\mathrm{H^+},i,t-h}} + \frac{K_{1,\mathrm{S(IV)}} K_{2,\mathrm{S(IV)}}}{\mathbf{m}^2_{\mathrm{H^+},i,t-h}} \right)$$

Dimensionless Henry's constant (19.37)

$$H'_{\mathrm{SO_2(aq)},i} = m_v c_w R^* T H_{\mathrm{SO_2}}$$

Growth/Aqueous Chemistry ODEs

Ratio of S(IV) to SO_2(aq) (19.38)

$$\frac{c_{\mathrm{S(IV)},i,t}}{c_{\mathrm{SO_2(aq)},i,t}} = \left(1 + \frac{K_{1,\mathrm{S(IV)}}}{\mathbf{m}_{\mathrm{H}^+,i,t-h}} + \frac{K_{1,\mathrm{S(IV)}}K_{2,\mathrm{S(IV)}}}{\mathbf{m}^2_{\mathrm{H}^+,i,t-h}}\right)$$

First and second dissociation constants of S(IV) (19.39)

$$K_{1,\mathrm{S(IV)}} = \frac{\mathbf{m}_{\mathrm{H}^+,i}\mathbf{m}_{\mathrm{HSO_3^-},i}\gamma^2_{i,\mathrm{H}^+/\mathrm{HSO_3^-}}}{\mathbf{m}_{\mathrm{SO_2(aq)},i}} \qquad (19.40)$$

$$K_{2,\mathrm{S(IV)}} = \frac{\mathbf{m}_{\mathrm{H}^+,i}\mathbf{m}_{\mathrm{SO_3^{2-}},i}\gamma^2_{i,\mathrm{H}^+/\mathrm{SO_3^{2-}}}}{\mathbf{m}_{\mathrm{HSO_3^-},i}\gamma^2_{i,\mathrm{H}^+/\mathrm{HSO_3^-}}}$$

Chemical Loss Term

Consider aqueous reactions of family (19.46 - 7)

$$S(IV) + H_2O_2(aq) + H^+ \longrightarrow S(VI) + 2H^+ + H_2O(aq)$$

$$S(IV) + HO_{2,T} \longrightarrow S(VI) + OH(aq) + 2H^+$$

These represent individual aqueous reactions (19.48-52)

$$HSO_3^- + H_2O_2(aq) + H^+$$

$$HSO_3^- + HO_2(aq)$$

$$SO_3^{2-} + HO_2(aq)$$

$$HSO_3^- + O_2^-$$

$$SO_3^{2-} + O_2^-$$

Chemical Loss Term

and their equilibrium partitioning (19.53-4)

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

$$HO_2(aq) \Leftrightarrow H^+ + O_2^-$$

Chemical Loss Term

Family Loss Rate (19.55)

$$L_{c,\mathrm{S(IV)},i,t} = k_a c_{\mathrm{S(IV)},i,t} c_{\mathrm{H_2O_2},i,t} c_{\mathrm{H}^+,i,t} + k_b c_{\mathrm{S(IV)},i,t} c_{\mathrm{HO}_{2,T},i,t}$$

Rate Coefficient for $S(VI)+H_2O_2(aq)+H^+$ (19.56)

$$k_a = k_{a,1}\alpha_{1,\mathrm{S(IV)}}$$

Mole fraction of S(IV) partitioned to HSO_4^- (19.57)

$$\alpha_{1,\mathrm{S(IV)}} = \frac{\mathbf{m}_{\mathrm{H}^+,i,t-h} K_{1,\mathrm{S(IV)}}}{\mathbf{m}^2_{\mathrm{H}^+,i,t-h} + \mathbf{m}_{\mathrm{H}^+,i,t-h} K_{1,\mathrm{S(IV)}} + K_{1,\mathrm{S(IV)}} K_{2,\mathrm{S(IV)}}}$$

Chemical Loss Term

Rate coefficient for $S(VI)+HO_2(aq)$ (19.58)

$$k_b = \left\lfloor k_{b,1}\alpha_{1,\mathrm{S(IV)}} + k_{b,2}\alpha_{2,\mathrm{S(IV)}} \right\rfloor \alpha_{0,\mathrm{HO}_{2,T}} + \left\lfloor k_{b,3}\alpha_{1,\mathrm{S(IV)}} + k_{b,4}\alpha_{2,\mathrm{S(IV)}} \right\rfloor \alpha_{1,\mathrm{HO}_{2,T}}$$

Mole fraction of S(IV) partitioned to SO_4^{2-} (19.59)

$$\alpha_{2,\mathrm{S(IV)}} = \frac{K_{1,\mathrm{S(IV)}}K_{2,\mathrm{S(IV)}}}{\mathbf{m}^2_{\mathrm{H}^+,i,t-h} + \mathbf{m}_{\mathrm{H}^+,i,t-h}K_{1,\mathrm{S(IV)}} + K_{1,\mathrm{S(IV)}}K_{2,\mathrm{S(IV)}}}$$

Mole fraction of $HO_{2,T}$ partitioned to $HO_2(aq)$ and O_2^- (19.60-1)

$$\alpha_{1,\mathrm{HO}_{2,T}} = \frac{K_{1,\mathrm{HO}_{2,T}}}{\mathbf{m}_{\mathrm{H}^+,i,t-h} + K_{1,\mathrm{HO}_{2,T}}} \qquad \alpha_{0,\mathrm{HO}_{2,T}} = \frac{\mathbf{m}_{\mathrm{H}^+,i,t-h}}{\mathbf{m}_{\mathrm{H}^+,i,t-h} + K_{1,\mathrm{HO}_{2,T}}}$$

Effect of Sparse-Matrix Reductions When Solving Growth/Aqueous ODEs

Dissolution/chemistry of 10 gases to 16 size bins, 11 species per bin.

Quantity	With Out Reductions	With Reductions
Order of matrix	186	186
Initial fill-in	34,596	1226
Final fill-in	34,596	2164
Decomp. 1	2,127,685	6333
Decomp. 2	17,205	1005
Backsub. 1	17,205	1005
Backsub. 2	17,205	973

Table 19.2