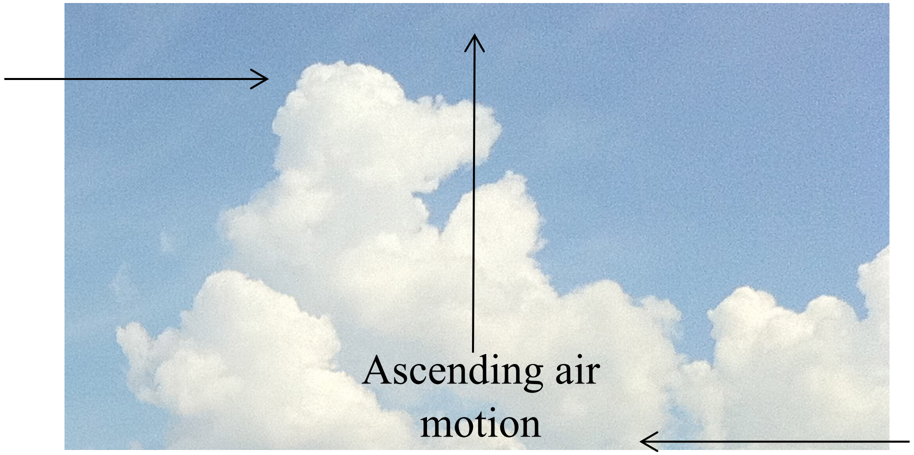
Clouds and Acid Rain

- General considerations on clouds and fogs
- Aqueous-phase chemistry
- Aqueous-phase chemical transformations
- Emission control strategies for acid rain



Clouds



Cloud top: evaporation

Ascending air motion

Cloud base: start of water vapor condensation

A cloud is formed when water vapor condenses on ultrafine particles (Aitken nuclei) and fine particles, and next on cloud droplets and ice crystals. Condensation occurs when the ascending air parcel cools adiabatically, which leads to a lower capacity to contain water vapor (i.e., increase in relative humidity): cloud base. When temperature and pressure are such that the relative humidity becomes less than 100 %, the cloud evaporates (cloud top). Therefore, there is constant air motion within a cloud.

Cumulus Clouds

Cumulus clouds are formed in presence of a strong vertical air motion (convection).

Stratus Clouds

Stratus clouds are formed when a moist air parcel rises and, while colling adiabatically, leads to the condensation of water vapor (since cold air has a lower capacity for water vapor content than warm air).

Precipitating Clouds: Nimbus Cumulonimbus and Nimbostratus

When cloud droplets increase in size, their fall velocity increases. If the cloud droplet fall velocity becomes greater than the vertical velocity of the ascending air parcel, the cloud droplet becomes a rain drop.

- A precipitating cumulus cloud is called a cumulonimbus.

- A precipitating stratus cloud is called a nimbostratus.

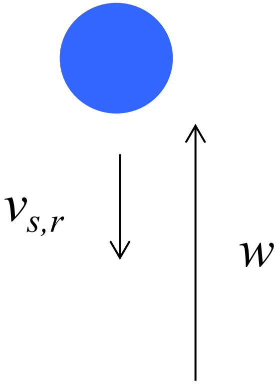
Precipitating and Non-precipitating Clouds

Non-precipitating cumulus cloud

Precipitating cumulonimbus

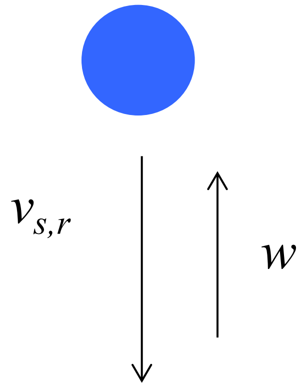
Precipitating and Non-precipitating Clouds

Non-precipitating cumulus cloud



The fall velocity of the cloud droplets, $v_{s,r}$, is less than the vertical velocity of the ascending air, w.

Precipitating and Non-precipitating Clouds



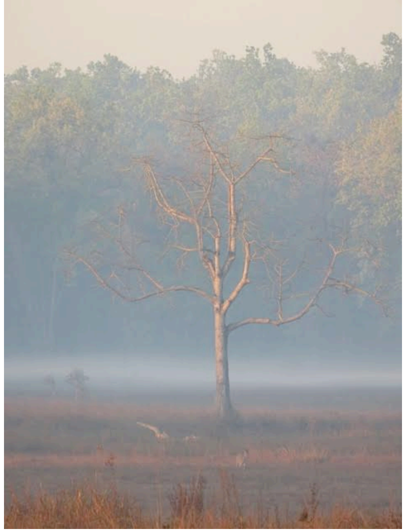
The fall velocity of the cloud droplets (raindrops), $v_{s,r}$, is greater than the vertical velocity of the ascending air, w.

Precipitating cumulonimbus

Fogs

Fog is a cloud that is in contact with the Earth's surface (visual range < 1 km)

Advection fog



Radiation fog

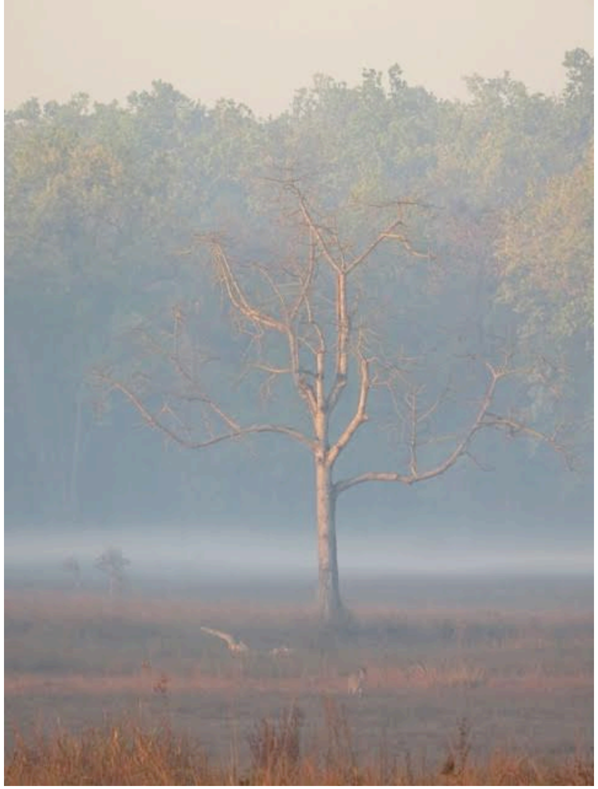
Fogs

Advection fog

An advection fog forms when a moist air parcel gets into contact with a cold surface, which leads to a decrease in the saturation vapor pressure of water vapor and its condensation (for example, summer fog in San Francisco, California, due to the upwelling coastal cold water of the Pacific Ocean).

Fogs

A radiation fog forms when the ambient temperature of a moist air parcel decreases sufficiently (for example at night), thereby leading to a decrease in the saturation vapor pressure of water vapor such that it reaches 100 % relative humidity (for example wintertime fogs in humid areas).



Radiation fog

Clouds and Fogs

- Liquid water contents (order of magnitude)
  - Cumulus: ~ 1 g/m^3
  - Cumulonimbus: > 1 g/m^3
  - Stratus: ~ 0.1 g/m^3
  - Nimbostratus: > 0.1 g/m^3
  - Fog: < 0.1 g/m^3

- Drops and droplets (order of magnitude of the mean diameter)
  - Non-precipitating cloud: ~ 40 μm
  - Rain: ~ 1 mm
  - Fog: ~ 10 μm

Atmospheric Particles

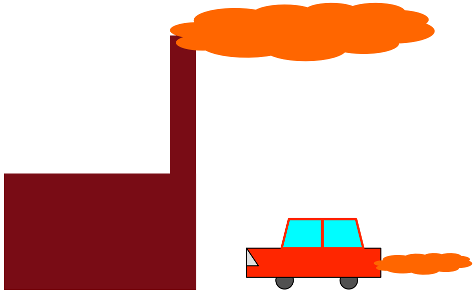
- Some particles (or fractions of particles) are formed by **chemical reaction** in the atmosphere from gases (sulfate, nitrate, ammonium, organic compounds…); these reactions can occur in the gas phase or **in the aqueous phase**: these are secondary particles or secondary PM.
- If the cloud evaporates, then some of the droplet chemical species form an atmospheric particle.

Nitric Acid Formation

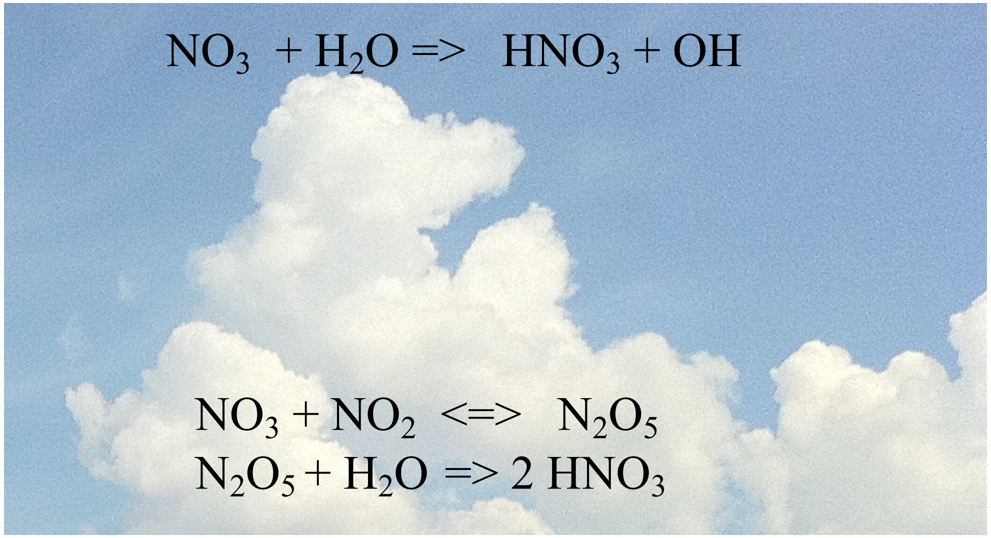
$NO_2 + O_3 \Rightarrow NO_3 + O_2$

$NO_2 + OH \Rightarrow HNO_3$

NO_x



Heterogeneous reactions in clouds



$NO_3 + H_2O \Rightarrow HNO_3 + OH$

$NO_3 + NO_2 \Leftrightarrow N_2O_5$

$N_2O_5 + H_2O \Rightarrow 2\,HNO_3$

Nitric Acid Formation
Daytime Gas Phase: OH

$$NO_2 + OH \Rightarrow HNO_3$$

These reactions are negligible at night because OH is not produced in the absence of sunlight (with the exceptions of alkene oxidation by O_3 and PAN reaction in presence of very high NO concentrations).

This reaction is not linear for $NO_2 \Rightarrow HNO_3$

A change of *x* % in NO_2 leads to a change in OH radical concentrations, which affects the reaction rate and, therefore, a change in nitric acid, which is not exactly *x* %.

$$k = 13600 \text{ ppm}^{-1} \text{ min}^{-1};\ v_r = k\,[NO_2]\,[OH]$$

$[OH] > 10^6$ cm^{-3} => the oxidation rate of NO_2 is on the order of 10 % per hour during a summer day.

Nitric Acid Formation
Nighttime Gas Phase: O_3

$NO_2 + O_3 \Rightarrow NO_3 + O_2$

$NO_3 + H_2O \Rightarrow HNO_3 + OH$

$NO_2 + NO_3 \Leftrightarrow N_2O_5$

$N_2O_5 + H_2O \Rightarrow 2\,HNO_3$

These reactions are negligible during the day because NO_3 is rapidly photolyzed:

$NO_3 + h\nu \Rightarrow NO_2 + O$; $NO_3 + h\nu \Rightarrow NO + O_2$

The hydrolysis reactions ($NO_3 + H_2O$ and $N_2O_5 + H_2O$) are much faster when they occur heterogeneously at the surface of droplets.

Nitric Acid Formation
Nighttime Gas Phase: O_3

$$NO_2 + O_3 \Rightarrow NO_3 + O_2$$

$$NO_3 + H_2O \Rightarrow HNO_3 + OH$$

$$NO_2 + NO_3 \Leftrightarrow N_2O_5$$

$$N_2O_5 + H_2O \Rightarrow 2\,HNO_3$$

This system of reactions is strongly non-linear for $NO_2 \Rightarrow HNO_3$

A change of *x* % in NO_2 leads to a change in O_3 concentrations, which affects the rate of the first reaction and, therefore, leads to a change in nitric acid, which is not exactly *x* % (it can be greater or less than *x*).

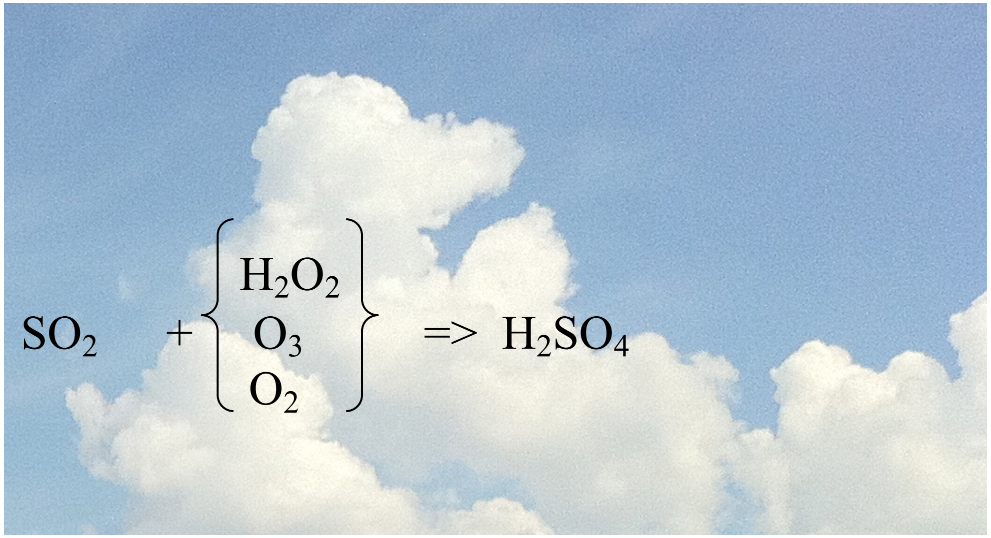
Nitric Acid Formation
Gas phase: Organic Compounds

$$NO_3 + RH \quad => \quad HNO_3 + R$$

These reactions are generally minor for the formation of HNO_3.

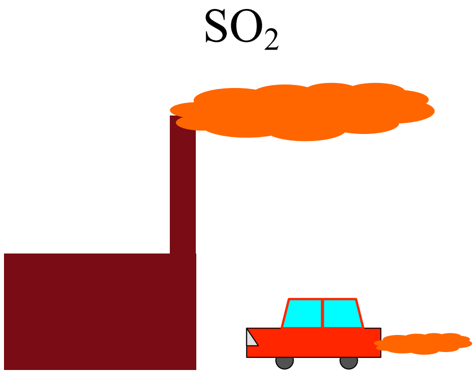
Sulfuric Acid Formation

System of non-linear reactions in clouds



$$SO_2 + \left\{ \begin{matrix} H_2O_2 \\ O_3 \\ O_2 \end{matrix} \right\} \Rightarrow H_2SO_4$$

$SO_2 + OH \Rightarrow H_2SO_4 + HO_2$



Sulfuric Acid Formation
Gas Phase: OH

$SO_2 + OH + M \Rightarrow HOSO_2 + M$

$HOSO_2 + O_2 \Rightarrow SO_3 + HO_2$

$SO_3 + H_2O + M \Rightarrow H_2SO_4 + M$

$SO_2 + OH \Rightarrow H_2SO_4 + HO_2$

$HO_2 + NO \Rightarrow OH + NO_2$

This system of reaction is linear for $SO_2 \Rightarrow H_2SO_4$

A change of x % in SO_2 leads to a change of x % in sulfuric acid.

Sulfuric Acid Formation
Gas Phase: OH

$$SO_2 + OH + M \Rightarrow HOSO_2 + M$$

$$HOSO_2 + O_2 \Rightarrow SO_3 + HO_2$$

$$SO_3 + H_2O + M \Rightarrow H_2SO_4 + M$$

$$SO_2 + OH \Rightarrow H_2SO_4 + HO_2$$

The first reaction governs the overall reaction rate because the following reactions are much faster. Therefore, the overall kinetics is governed by the rate of the first reaction:

$$k = 1400 \text{ ppm}^{-1} \text{ min}^{-1} \; ; \; v_r = k\,[SO_2]\,[OH]$$

$[OH] > 10^6$ cm^{-3} => the oxidation rate of SO_2 is on the order of 1 % per hour during a summer day.

Atmospheric Aqueous Phase Concentration and Activity

Concentration of a chemical species in the aqueous phase:

- Molar fraction: number of moles per mole of water (x_i)
- Molality: number of moles per kg of water (m_i)
- Molarity: number of moles per liter of water (c_i)

Therefore, for trace pollutants: $m_i \sim c_i$

Activity of a chemical species in a non-ideal solution:

$$\alpha_i = \gamma_i \, x_i$$

where:

x_i = molar fraction

α_i = activity

γ_i = activity coefficient; it represents the deviation of the solution with respect to an ideal solution.

Atmospheric Aqueous Phase Concentration and Activity

Activity of a chemical species in a non-ideal solution:

$$\alpha_i = \gamma_i x_i$$

For a cloud droplet, one may assume that the solution is ideal because the concentrations of chemical species (other than water) are small:

$$\gamma_i = 1 \text{ and } \alpha_i = x_i$$

However, for a small particle, the solution will not be ideal because the concentrations of chemical species will be high.

Atmospheric Aqueous Phase Equilibrium with the Gas Phase

$$A(g) \iff A(aq)$$

Henry's law (dilute solution):

$$[A(aq)] = H_A \, P_A$$

$[A(aq)]$: molarity of A (moles per liter or M)
P_A: partial pressure of A (atm)
H_A: Henry's law constant ($M\ atm^{-1}$)

Important points:

- The Henry's law constant can be defined with other units and is sometimes defined as the inverse ratio (concentration in the gas phase / concentration in the aqueous phase).
- Henry's law is valid only for species present in low concentrations.

Effective Henry's Law Constant
Monoacid: HNO_3

Gas/water equilibrium $HNO_3(g) <=> HNO_3(aq)$

Dissociation equilibrium $HNO_3(aq) <=> NO_3^- + H^+$

Equilibrium constants:

$[HNO_3(aq)] = H_{HNO3} P_{HNO3}$
$[NO_3^-] [H^+] / [HNO_3(aq)] = K_{HNO3}$

$[HNO_3(aq)]$, $[NO_3^-]$, $[H^+]$: molarities (M)
P_{HNO3}: partial pressure of NO_3 (atm)
H_{HNO3}: Henry' s law constant ($M\ atm^{-1}$)
K_{HNO3}: dissociation constant of acid HNO_3 (M)

Effective Henry's Law Constant Monoacid: HNO_3

One defines the effective Henry's law constant, $H_{\mathrm{HNO3},\,\mathit{eff}}$, as the equilibrium between the species in the gas phase and all corresponding species in the aqueous phase:

$$[\mathrm{HNO_3(aq)}] + [\mathrm{NO_3^-}] = H_{\mathrm{HNO3},\,\mathit{eff}}\,P_{\mathrm{HNO3}}$$

Substituting:

$$[\mathrm{HNO_3(aq)}] + ([\mathrm{HNO_3(aq]}\ K_{\mathrm{HNO3}} / [\mathrm{H^+}]) = H_{\mathrm{HNO3},\,\mathit{eff}}\,P_{\mathrm{HNO3}}$$

$$[\mathrm{HNO_3(aq)}]\ (1 + K_{\mathrm{HNO3}} / [\mathrm{H^+}]) = H_{\mathrm{HNO3},\,\mathit{eff}}\,P_{\mathrm{HNO3}}$$

$$H_{\mathrm{HNO3},\,\mathit{eff}} = H_{\mathrm{HNO3}}\ (1 + K_{\mathrm{HNO3}} / [\mathrm{H^+}])$$

Effective Henry's Law Constant
Diacid: Sulfuric Acid (H_2SO_4)

This equation can be generalized in the case of a second dissociation (for diacids such as sulfuric acid).

Gas/water equilibrium $H_2SO_4(g) <=> H_2SO_4(aq)$

Dissociation equilibria

$H_2SO_4(aq) <=> HSO_4^- + H^+$ K_1
$HSO_4^-(aq) <=> SO_4^{2-} + H^+$ K_2

Effective Henry's law constant:

$$H_{\mathrm{H2SO4,\ eff}} = \mathrm{H}_{\mathrm{H2SO4}} (1 + (K_1 / [\mathrm{H}^+]) + (K_1 K_2 / ([\mathrm{H}^+]^2))$$

Effective Henry's Law Constants Bases and Acids

One can also define effective Henry's law constants for bases (for example, for ammonia, NH_3).

The effective Henry's law constant depends on pH.

For an acid, it decreases as the pH decreases (less dissociation of acids in an acidic solution).

For a base, it increases as the pH decreases (more dissociation of bases in an acidic solution).

Solubility of some Air Pollutants

Chemical species	**Henry's law constant (M atm^{-1})**	**Effective Henry's law constant[a] (M atm^{-1})**	**Fraction in the aqueous phase**
NO	1.9×10^{-3}	1.9×10^{-3}	0.000005 %
NO_2	1.2×10^{-2}	1.2×10^{-2}	0.00002 %
O_3	1.1×10^{-2}	1.1×10^{-2}	0.00002 %
CO_2	3.4×10^{-2}	4×10^{-2}	0.0001 %
SO_2	1.23	6.5×10^{3}	14 %
NH_3	62	2.6×10^{5}	87 %
HCHO[b]	6.3×10^{3}	6.3×10^{3}	13 %
H_2O_2	7.45×10^{4}	7.45×10^{4}	65 %
HNO_3	2.1×10^{5}	1.3×10^{12}	100 %

(a) pH = 5.6; $LWC = 1$ g/m^3; $T = 25$ ° C; (b) including diol formation

$H < 10^3$ M atm^{-1}
not soluble

$10^3 < H < 10^5$
soluble

$H > 10^5$
very soluble

Dissociation Equilibrium of Water

$$H_2O(l) \leftrightarrow H^+ + OH^-$$

H^+ is the hydrogen ion (proton);
OH^- is the hydroxide ion

$$K'_{H_2O} = \frac{[H^+][OH^-]}{[H_2O(l)]} = 1.82 \text{ x } 10^{-16} \text{ M}$$

$$K_{H_2O} = [H^+][OH^-] = 10^{-14} \text{ M}^2$$

$$\text{pH} = -\log\left(\gamma_{H^+}[H^+]\right)$$

pH = 7.0 for pure water at 298 K

Atmospheric Aqueous Phase

$$\left.\begin{array}{lll} CO_2(g) & <=> & CO_2(aq) \\ CO_2(aq) + H_2O(l) & <=> & H_2CO_3 \end{array}\right\} \quad H = 3.4 \text{ x } 10^{-2} \text{ M atm}^{-1}$$

H_2CO_3 <=> $HCO_3^- + H^+$ $K = 4.3 \text{ x } 10^{-7}$ M

HCO_3^- <=> $CO_3^{2-} + H^+$ $K = 4.7 \text{ x } 10^{-11}$ M

H_2O <=> $H^+ + OH^-$ $K = 10^{-14}$ M^2

Electroneutrality equation of the aqueous phase:

$$[H^+] = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-]$$

Atmospheric Aqueous Phase

The concentration of carbon dioxide is currently about 400 ppm

The pH of water in clouds can be calculated from the atmospheric concentration of CO_2: it it about 5.6.

Dissolution of SO_2 in the Aqueous Phase

$$\left.\begin{array}{lcl} SO_2(g) & <=> & SO_2(aq) \\ SO_2(aq) + H_2O(l) & <=> & H_2SO_3 \end{array}\right\} \quad H = 1.23 \text{ M atm}^{-1}$$

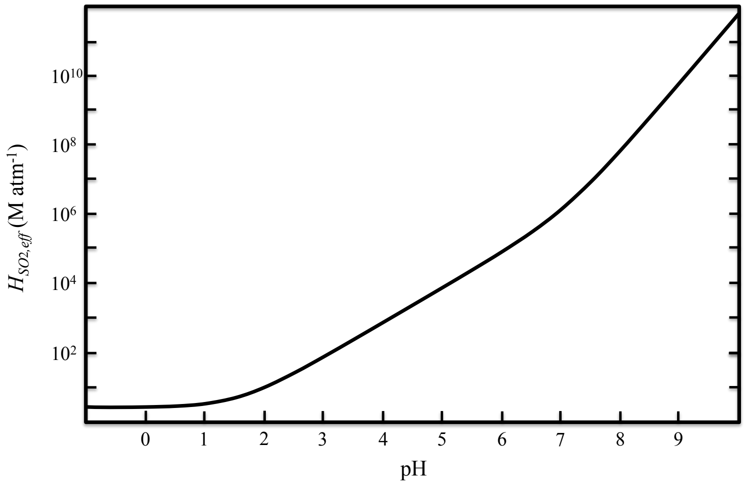
$$H_2SO_3 \quad <=> \quad HSO_3^- + H^+ \qquad K_1 = 1.3 \text{ x } 10^{-2} \text{ M}$$

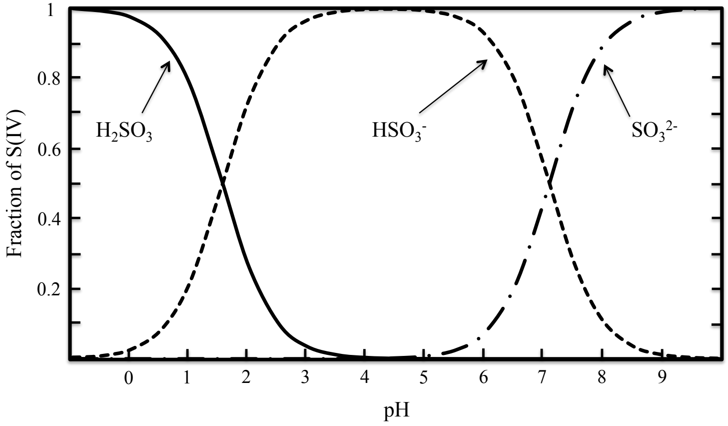
$$HSO_3^- \quad <=> \quad SO_3^{2-} + H^+ \qquad K_2 = 6.6 \text{ x } 10^{-8} \text{ M}$$

SO_2 is a weak acid: it is not completely dissociated in the aqueous phase

$$[S(IV)] = [H_2SO_3] + [HSO_3^-] + [SO_3^{2-}]$$

Dissolution of SO_2 in the Aqueous Phase





$$[\mathrm{S(IV)(aq)}] = H_{\mathrm{eff}}\ P_{\mathrm{SO_2}}$$

$$H_{eff} = H\left(1+\frac{K_1}{[\mathrm{H^+}]}+\frac{K_1 K_2}{[\mathrm{H^+}]^2}\right)$$

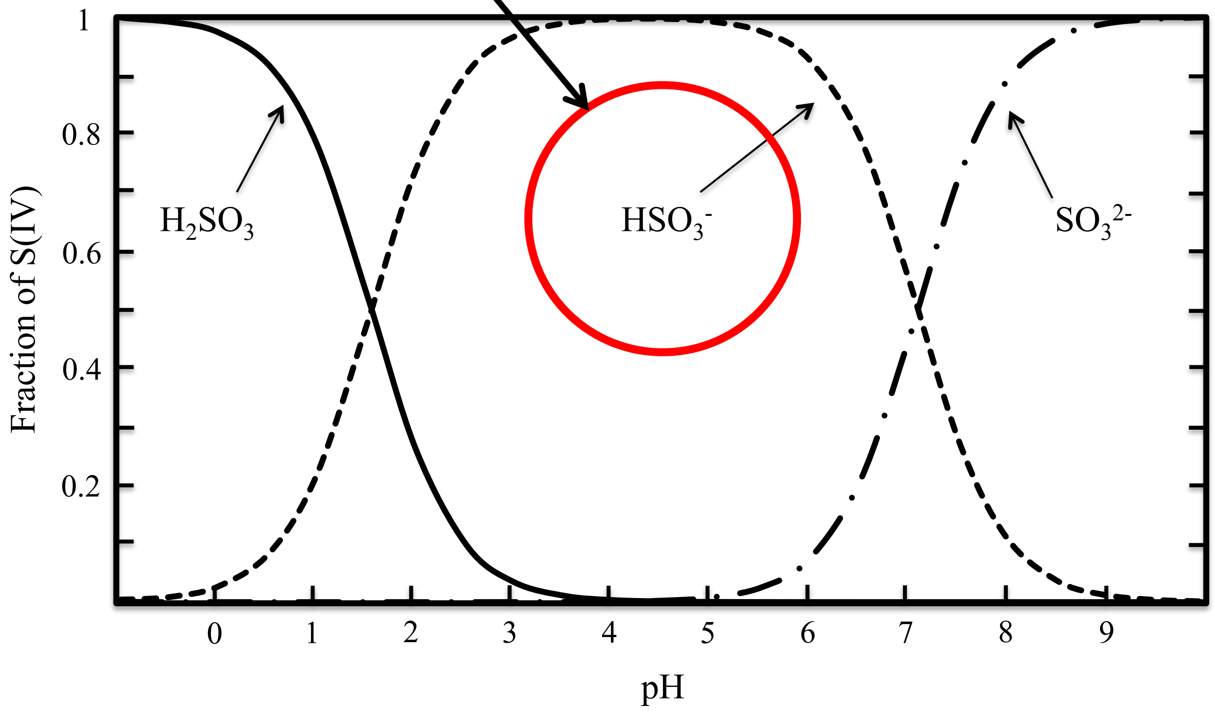
$$\frac{[\mathrm{H_2SO_3(aq)}]}{[\mathrm{S(IV)(aq)}]} = \left(1+\frac{K_1}{[\mathrm{H^+}]}+\frac{K_1 K_2}{[\mathrm{H^+}]^2}\right)^{-1}$$

$$\frac{[\mathrm{HSO_3^-(aq)}]}{[\mathrm{S(IV)(aq)}]} = \left(1+\frac{[\mathrm{H^+}]}{K_1}+\frac{K_2}{[\mathrm{H^+}]}\right)^{-1}$$

$$\frac{[\mathrm{SO_3^{2-}(aq)}]}{[\mathrm{S(IV)(aq)}]} = \left(1+\frac{[\mathrm{H^+}]^2}{K_1 K_2}+\frac{[\mathrm{H^+}]}{K_2}\right)^{-1}$$

Dissolution of SO_2 in the Aqueous Phase

Range of pH values in atmospheric clouds: HSO_3^- is the major species



Dissolution of H_2SO_4 in the Aqueous Phase

$$H_2SO_4 \iff HSO_4^- + H^+$$

$$HSO_4^- \iff SO_4^{2-} + H^+$$

H_2SO_4 is a strong acid: it dissociates easily in the aqueous phase.

$$[S(VI)] = [H_2SO_4] + [HSO_4^-] + [SO_4^{2-}]$$

Sulfuric Acid Formation
Aqueous Phase: H_2O_2

$$HSO_3^- + H_2O_2 \Rightarrow HSO_4^- + H_2O$$

This reaction does not depend much on pH.

The rate of this reaction is fast and the lifetime of SO_2 is on the order of only a few minutes: it is a titration reaction.

$H = 7.4 \times 10^4$ M / atm for H_2O_2

$$\frac{d[H_2SO_4]}{dt} = 7.2 \times 10^7 \; [H^+]\,[S(IV)]\,[H_2O_2] \qquad M\,s^{-1}$$

Sulfuric Acid Formation
Aqueous Phase: H_2O_2

$$SO_2 + H_2O_2 \quad\Rightarrow\quad H_2SO_4$$

If $[SO_2] < [H_2O_2]$: a change of x % in SO_2 leads to a change of x % in sulfuric acid and the system is linear.

If $[SO_2] > [H_2O_2]$: a change of x % in SO_2 leads to a change of 0 % in sulfuric acid as long as $[SO_2] > [H_2O_2]$ and the system is non-linear; the reaction stops when H_2O_2 has been totally consumed: one says that the system is oxidant-limited.

Sulfuric Acid Formation
Aqueous Phase: O_3

$H_2SO_3 + O_3 \Rightarrow H_2SO_4 + O_2 \qquad k = 2.4 \times 10^4\ M^{-1}\ s^{-1}$

$HSO_3^- + O_3 \Rightarrow HSO_4^- + O_2 \qquad k = 3.7 \times 10^5\ M^{-1}\ s^{-1}$

$SO_3^{2-} + O_3 \Rightarrow SO_4^{2-} + O_2 \qquad k = 1.5 \times 10^9\ M^{-1}\ s^{-1}$

$S(IV) + O_3 \Rightarrow S(VI)$

$H_{O3} = 1.1 \times 10^{-2}$ M/atm

This reaction depends strongly on pH.

The overall reaction rate is fast but the lifetime of SO_2 is on the order of several tens of minutes; therefore, it is typically slower that the oxidation by H_2O_2.

Sulfuric Acid Formation
Aqueous Phase: O_3

$SO_2 + O_3 \Rightarrow H_2SO_4$

When H_2SO_4 is formed, the pH decreases (more acidic solution), the rate slows down and H_2SO_4 formation decreases => this reaction is self-limiting.

Therefore, a decrease of x % in SO_2 does not lead to a change of x % in sulfuric acid, but to a lesser decrease.

Sulfuric Acid Formation
Aqueous Phase: O_2

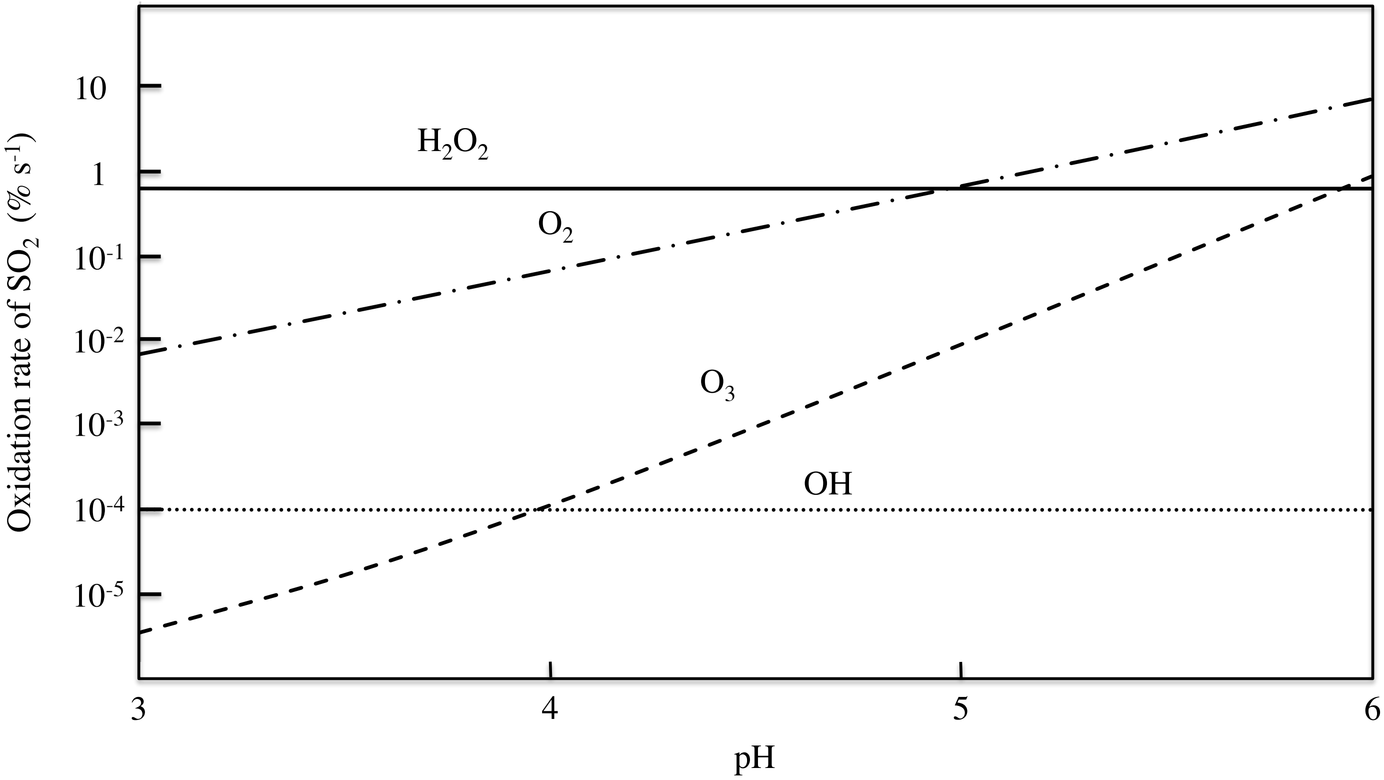
S(IV) (+ Mn^{2+}, Fe^{3+}) => S(VI)

This reaction is catalyzed by metal ions such as Fe^{3+} and Mn^{2+}.

The overall reaction rate is fast only when pH > 4; the kinetics slows down when the pH decreases and, therefore, this reaction is self-limiting.

Therefore, a decrease of *x* % in SO_2 does not lead to a change of *x* % in sulfuric acid, but to a lesser decrease.

Aqueous-phase Chemistry Kinetics of SO_2 Oxidation



Conditions for the cloud aqueous phase are as follows: the cloud is at about 3 km altitude, *P* = 0.69 atm, *T* = 5 ° C, *L* = 0.5 g m^{-3}. Conditions for the gas phase are as follows: *P* = 1 atm, *T* = 25 ° C, clear sky. Concentrations are as follows: $[SO_2(g)]$ = 2 ppb, $[H_2O_2(g)]$ = 2 ppb, $[O_3(g)]$ = 40 ppb, [Fe(aq)] = 10 mM, [Mn(aq)] = 0,5 mM, [OH(g)] = 10^6 cm^{-3}.

Aqueous-phase Chemistry
Kinetics of SO_2 Oxidation

- In an acidic solution, oxidation by H_2O_2 is the only important oxidation pathway.
- Oxidation by ozone and oxygen is self-limiting because the formation of sulfuric acid leads to a decrease in pH and, therefore, the kinetics slows down.
- Gas-phase oxidation by OH is very slow.

Emission Control Strategies for Acid Rain

- Acid rain is due mostly to sulfuric acid (H_2SO_4) and nitric acid (HNO_3).

- The formation of H_2SO_4 is dominated by aqueous-phase chemistry because its gas-phase chemistry is slow. The reduction of SO_2, precursor of H_2SO_4, may be strongly non-linear if the SO_2 concentrations are greater than the H_2O_2 concentrations (i.e., in an oxidant-limited regime). It will be almost linear once the SO_2 concentrations become less than the H_2O_2 concentrations (some non-linearity remains due to the pH dependency of the O_3 and O_2 reactions).

- The reduction of the precursors of HNO_3 may lead to a non-linear response of nitric acid formation, because it also affects oxidant concentrations (via the VOC/NO_x ratio of photochemical smog formation).