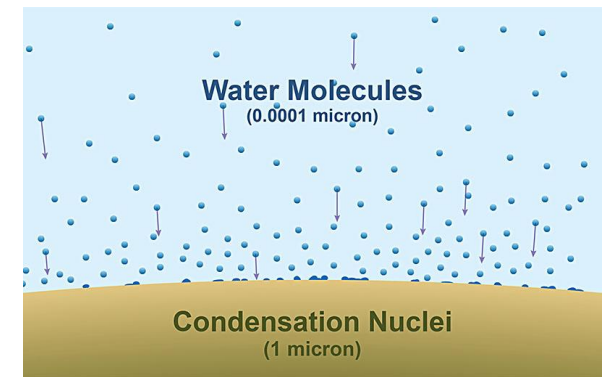


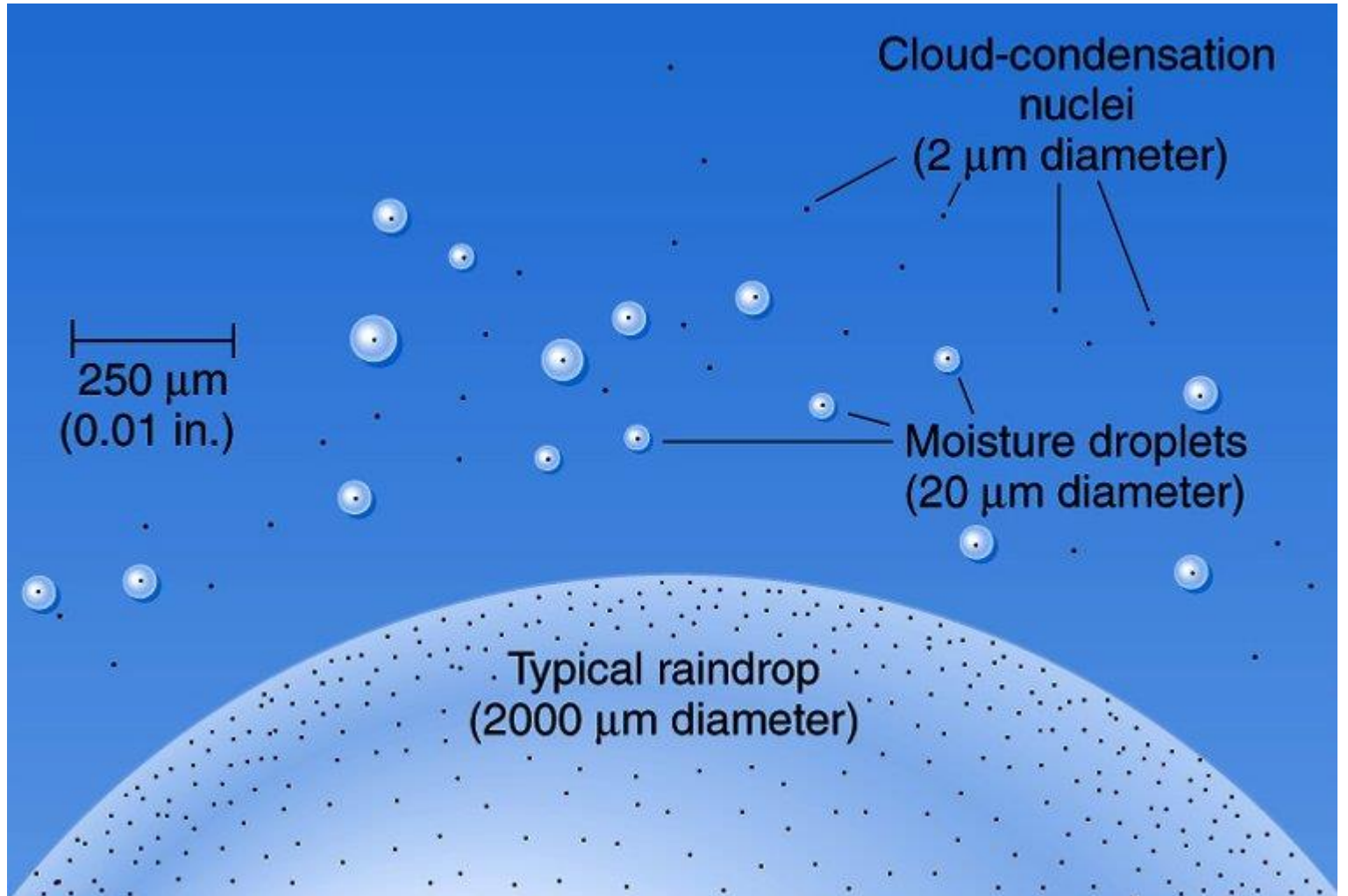
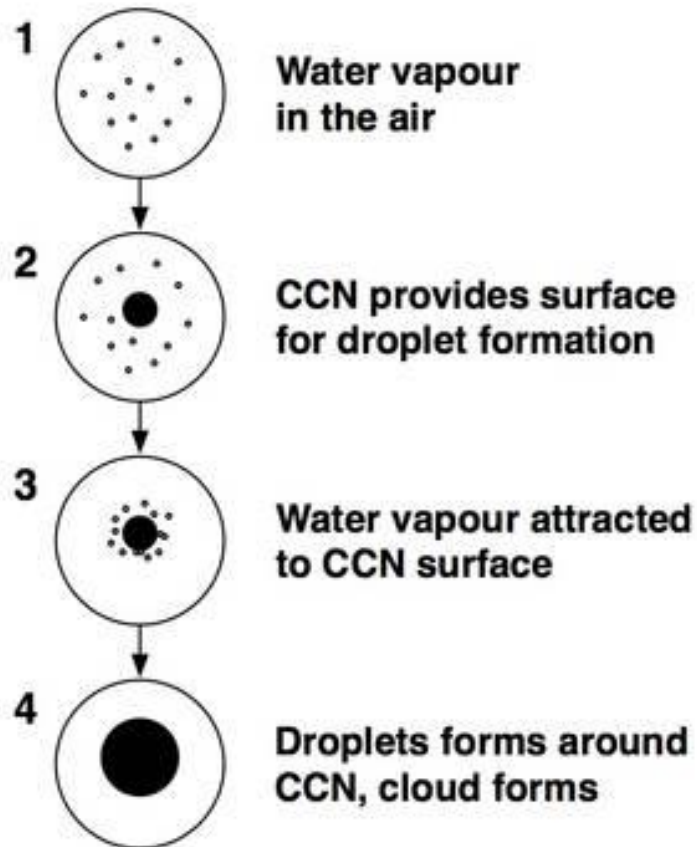
Tropospheric Chemistry - Precipitation

1. Water aerosol formation (clouds, fog, rain, snow)
2. Chemistry of gases in water
→ K_H and K_a
3. Composition of rainwater
4. Mechanisms of HNO_3 and H_2SO_4 production
5. Emission controls and abatement technology



1. Water aerosol formation

Cloud Condensation Nuclei (CCN)



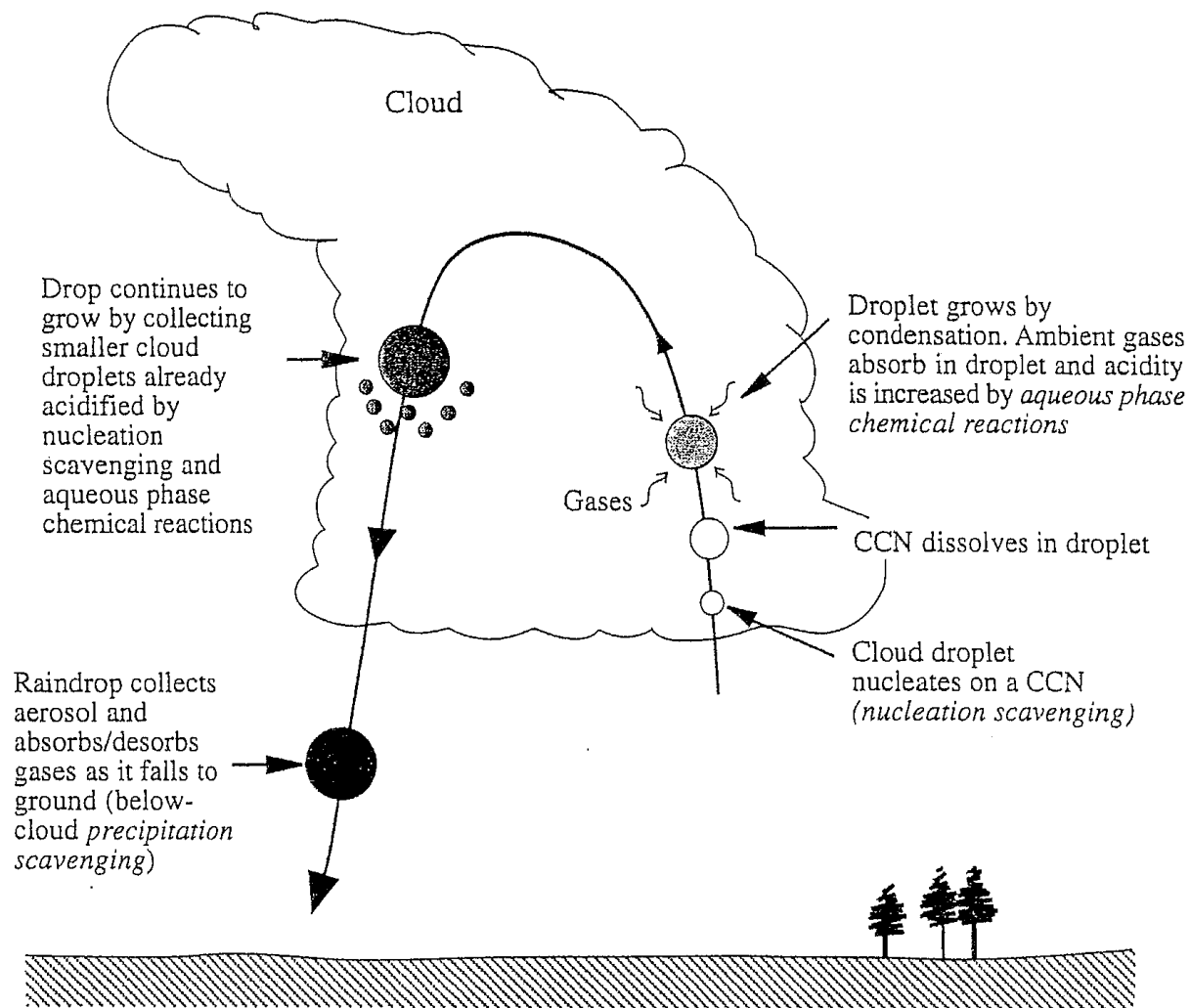


Figure 7.1. Schematic diagram of the processes affecting the chemical compositions of cloud droplets and rain. Not drawn to scale.

CCNs

Dust

Soot

Clay

Sea salt

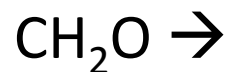
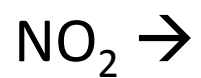
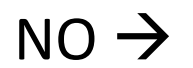
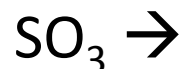
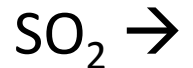
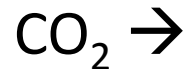
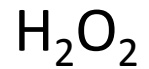
Phytoplankton

Microbes

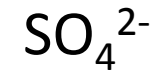
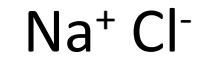
SVOCs

AgNO₃/AgI

Dissolved gases



Inorganic salts



Ground level clouds: Fog

→ enriched conc of dissolved ions



Water aerosol droplets evaporate

Closer to land based sources (e.g., NO_x, SO_x)

Oxidation rxns enhanced by presence of

O₃

R-O-O (VOCs and BVOCs)

2. Chemistry of gases in water

Dissolution governed by Equilibrium: Henry's Law

Conc (aq) proportional to Partial pressure of gas

$$X_{(g)} \rightleftharpoons X_{(aq)}$$

$$K_H = [X_{(aq)}] / P_{X(g)}$$

$$[X_{(aq)}] = K_H P_{X(g)}$$

Henry's Law Constants

M atm^{-1} or M Pa^{-1}

(watch out for the units!)

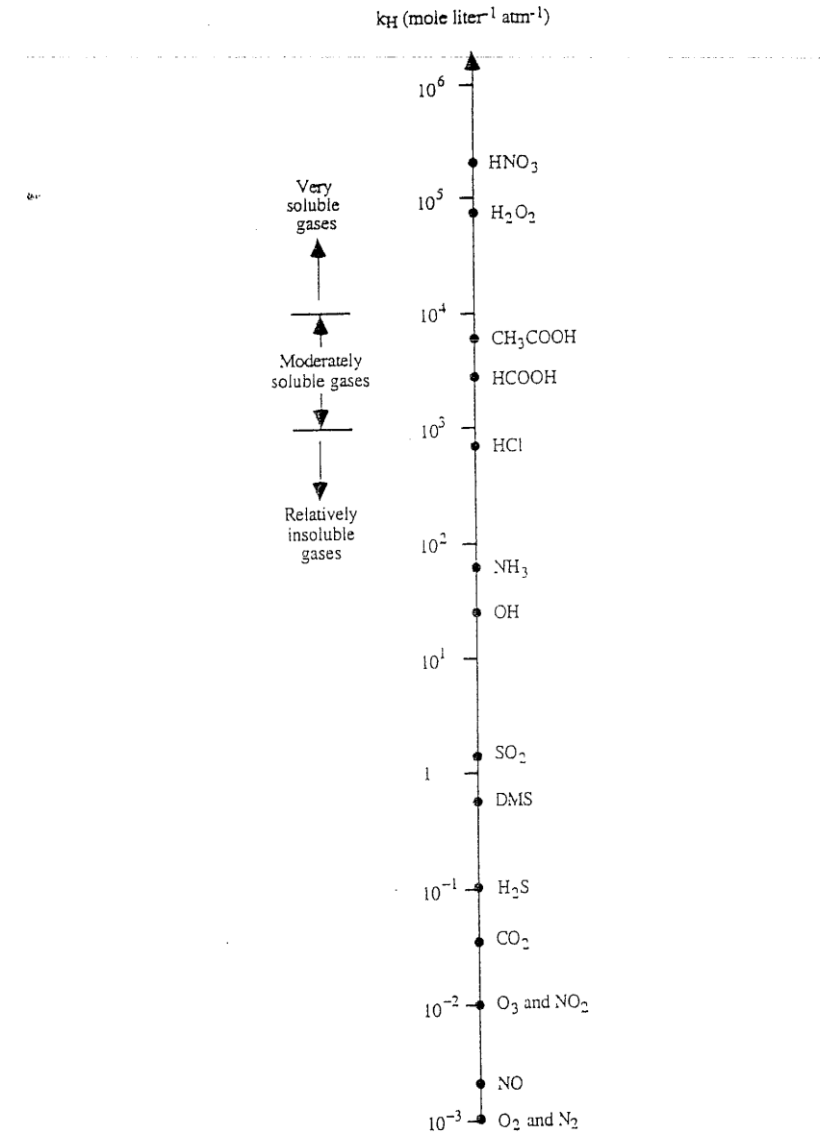


Figure 7.4. Values of the Henry's law constant (k_H) for some atmospheric gases in water at 25°C. These values account for the physical solubility of the gas only; any hydrolysis or other chemical reactions in the aqueous phase are not accounted for by these values. (The temperature dependence of k_H is discussed in Section 4.3 of Hobbs (2000). See Appendix VI.)

3. Composition of Rain

Typical chemical composition of precipitation in $\mu\text{equiv/L}$ *

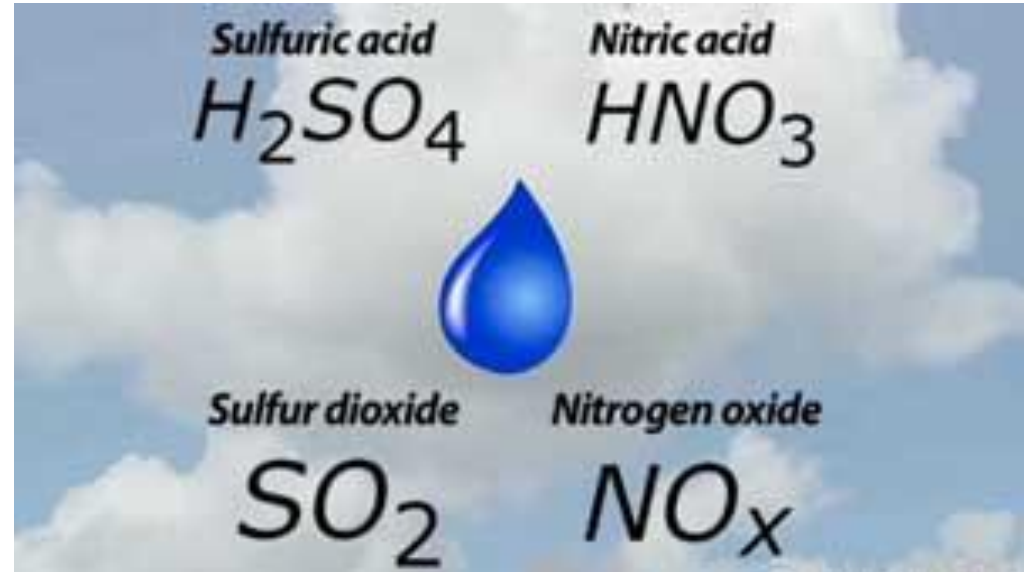
* concentrations reported as $\mu\text{equiv/L} = \mu\text{mol/L} \times \text{\#equiv/mol}$, where an equivalent is defined on the basis of charge (i.e., for divalent ions, there are 2 equivs per mol)

$$\text{for } \text{SO}_4^{2-} = 245 \mu\text{mol/L} \times 2 \text{ equiv/mol} = 490 \mu\text{equiv/L}$$

	Alaska Rainfall	California Rainfall	Bay of Fundy Fog
SO_4^{2-}	10	19	490
NO_3^-	2	24	160
Cl^-	5	22	61
Mg^{2+}	1	5	50
Na^+	2	20	22
K^+	1	1	78
Ca^{2+}	1	8	31
NH_4^+	2	19	50
pH	4.96	4.72	3.52

Acidic Rainfall

- Lowest recorded pH ~ 2.1
- pH $< 3-4$ not uncommon
- Past two decades $[\text{SO}_4^{2-}]$ decreasing, but $[\text{NO}_3^-]$ increasing



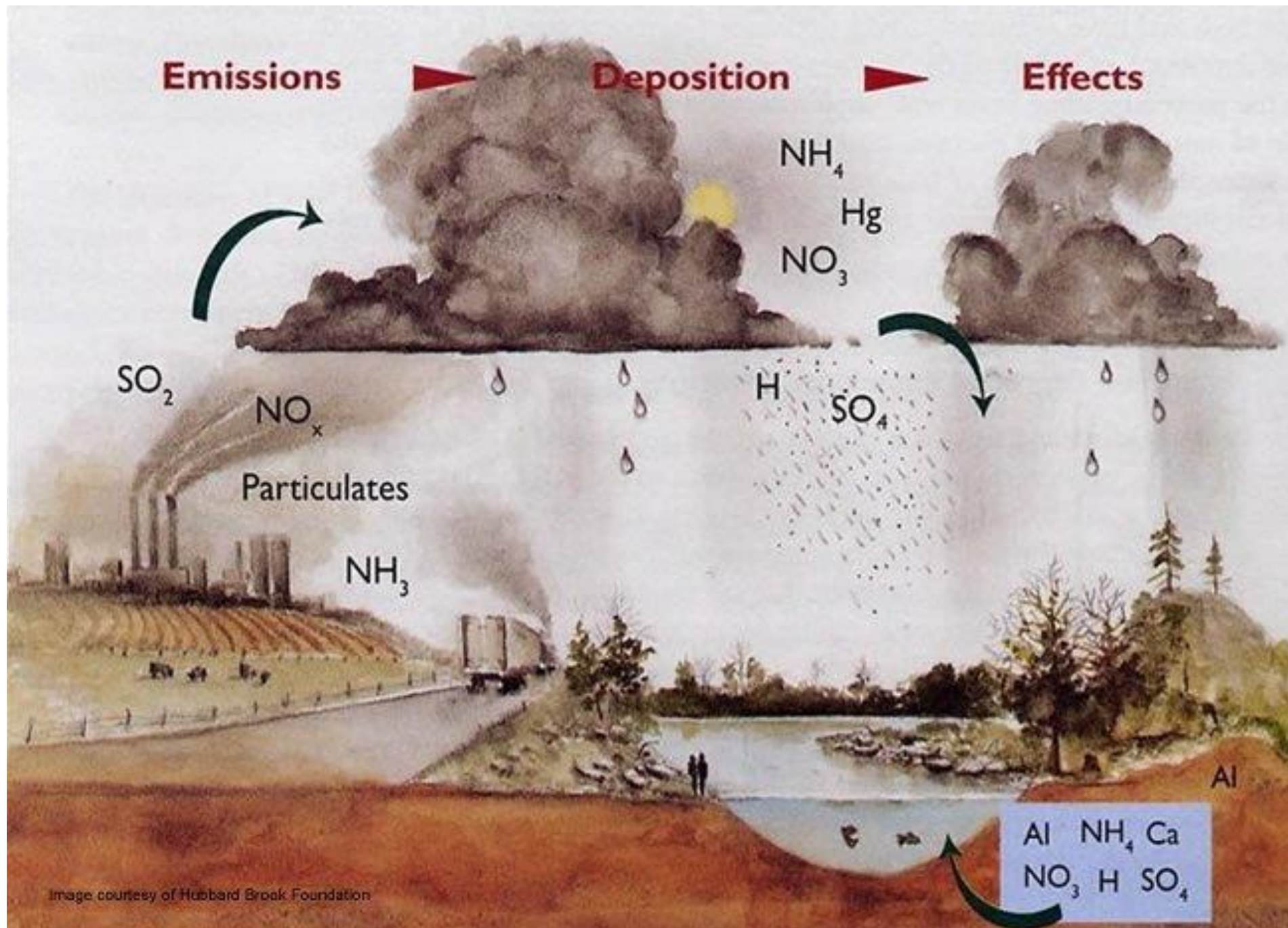
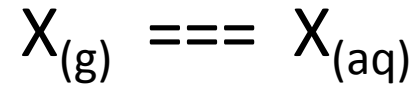


Image courtesy of Hubbard Brook Foundation

Chemistry of gases in water (continued)

Dissolution governed by Equilibrium: Henry's Law

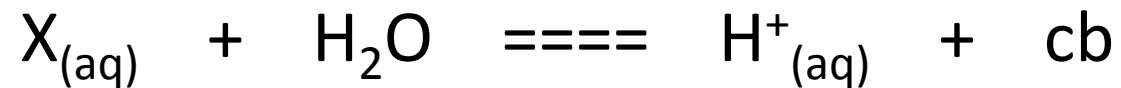
Conc (aq) proportional to Partial pressure of gas



$$K_H = [X_{(aq)}] / P_{X(g)}$$

$$[X_{(aq)}] = K_H P_{X(g)}$$

For acidic gases;



$$K_a = ([H^+][cb]) / [X_{(aq)}]$$

$$[H^+] = \sqrt{K_{a1} K_H P_{X(g)}}$$

Influence of covalent oxides on pH of rain

Consider;

1. **CO₂** at pre-industrial concentrations of 280 ppm_v

2. **CO₂** at current 400 ppm_v

3. **SO₂** at 10 ppb_v

Henry's Law & Ka Constants at 25 °C
(van Loon)

$$K_H (\text{CO}_2) = 3.3 \times 10^{-7} \text{ M Pa}^{-1}$$

$$K_{a1} (\text{CO}_2) = 4.5 \times 10^{-7}$$

$$K_H (\text{SO}_2) = 1.2 \times 10^{-5} \text{ M Pa}^{-1}$$

$$K_{a1} (\text{SO}_2) = 1.7 \times 10^{-2}$$

Seasonal pH variations in temperate climate

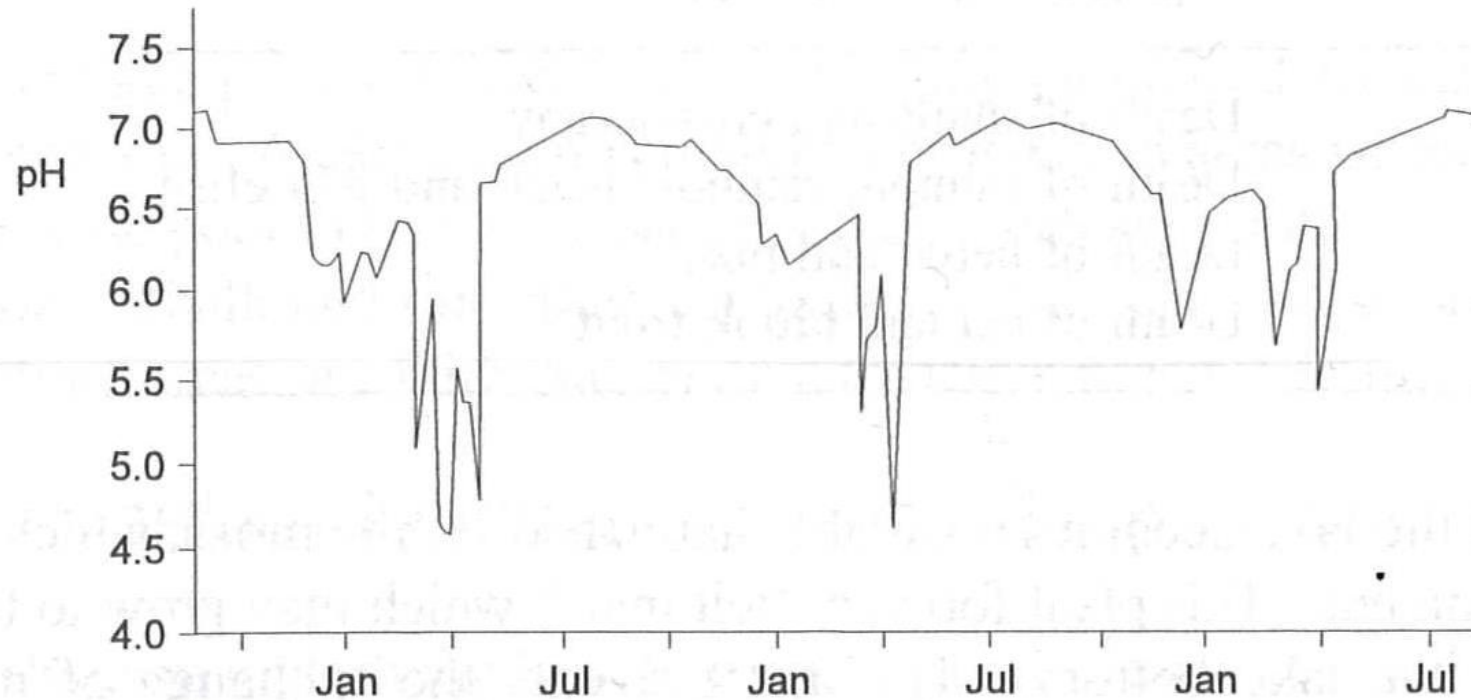


Figure 6.5: pH variation of an Adirondack lake during spring run-off; reproduced from Reference 26.

Why does acid rain matter?



Affects both

Natural

&

Built



environments



Acid Rain Affects

Human health



SO₂ – respiratory, heart and lung disease
Contributes PM

Aquatic Life



Terrestrial Life



Water Chemistry – increased metal/nutrient concentrations

Soil Chemistry – decreased metal/nutrient concentrations

Elevated Aluminium Concentrations

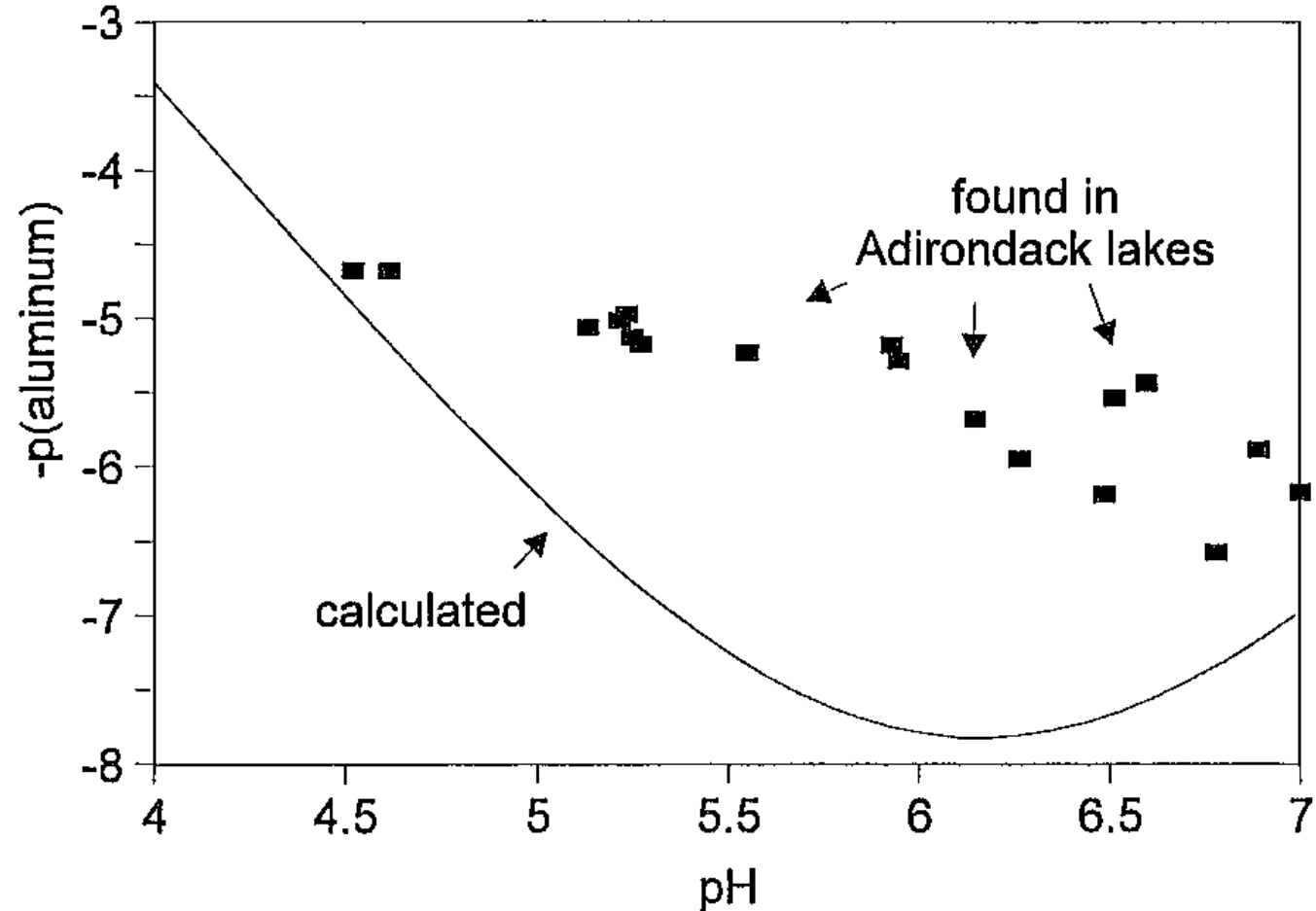


Figure 6.7: Calculated solubility of $\text{Al}(\text{OH})_3(\text{s})$ as a function of pH.

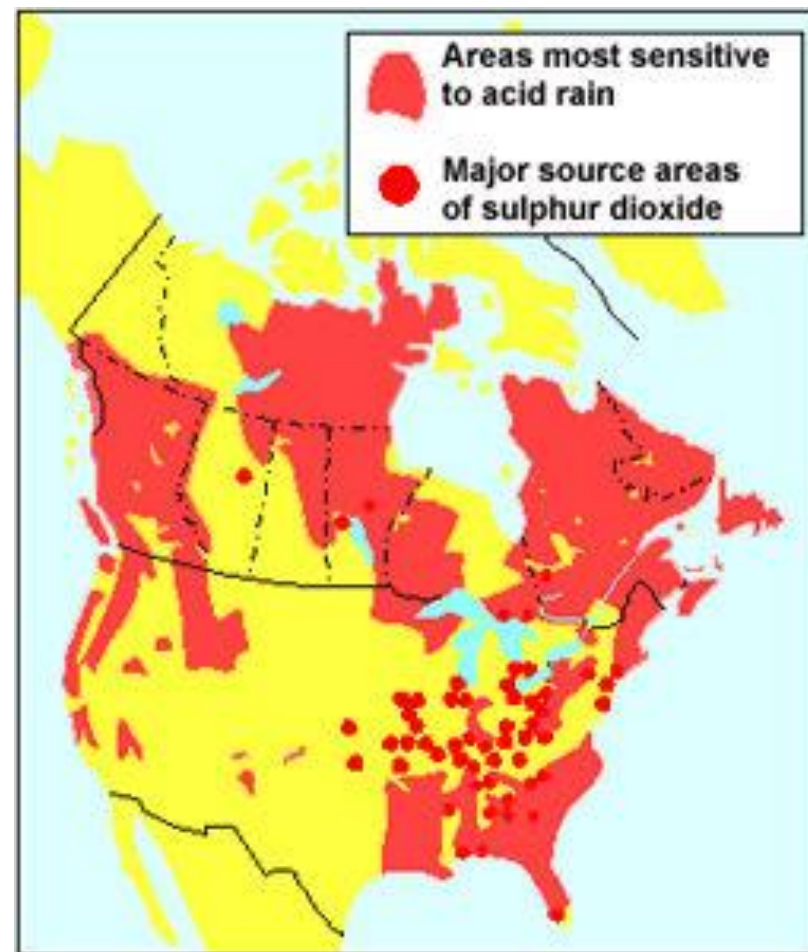
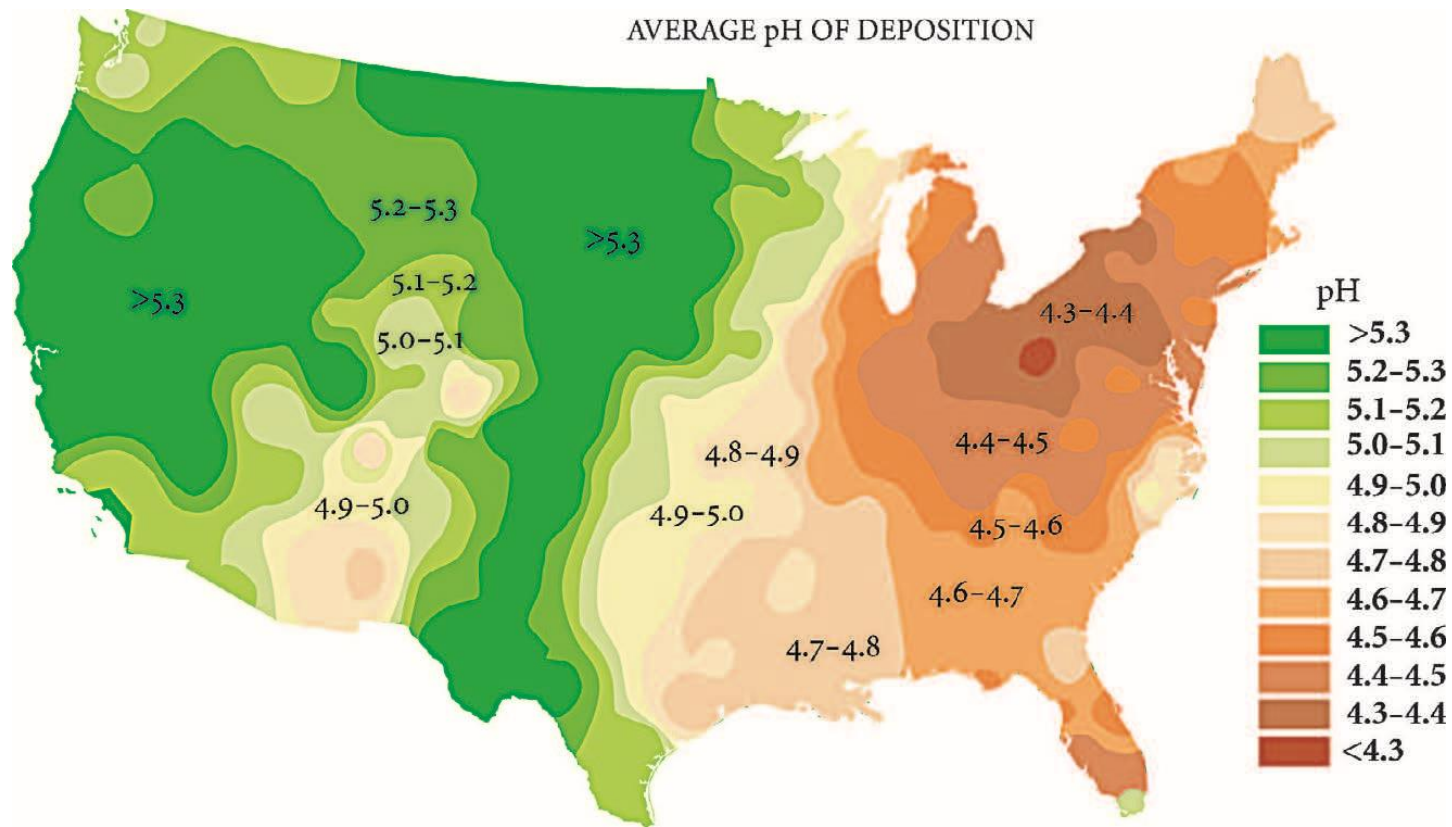
Table 6.2: Metal content of some ponds in the Smoking Hills (Canada).

Distance ^a	40	190	670	4400
pH	1.8	2.8	3.6	8.1
Acidity ^b	0.12	6.4×10^{-3}	6×10^{-4}	-
Alkalinity ^b	-	-	-	1×10^{-3}
SO ₄ ²⁻ , ppm	16,000	380	160	110
Be, ppm	230	40	-	-
Mg, ppm	500	22	13	42
Al, ppm	590	18	3.8	-
Ca, ppm	370	45	49	61
Mn, ppm	64	2.8	3.5	-
Fe, ppm	2600	32	1.1	0.04
Ni, ppm	22	0.2	0.06	

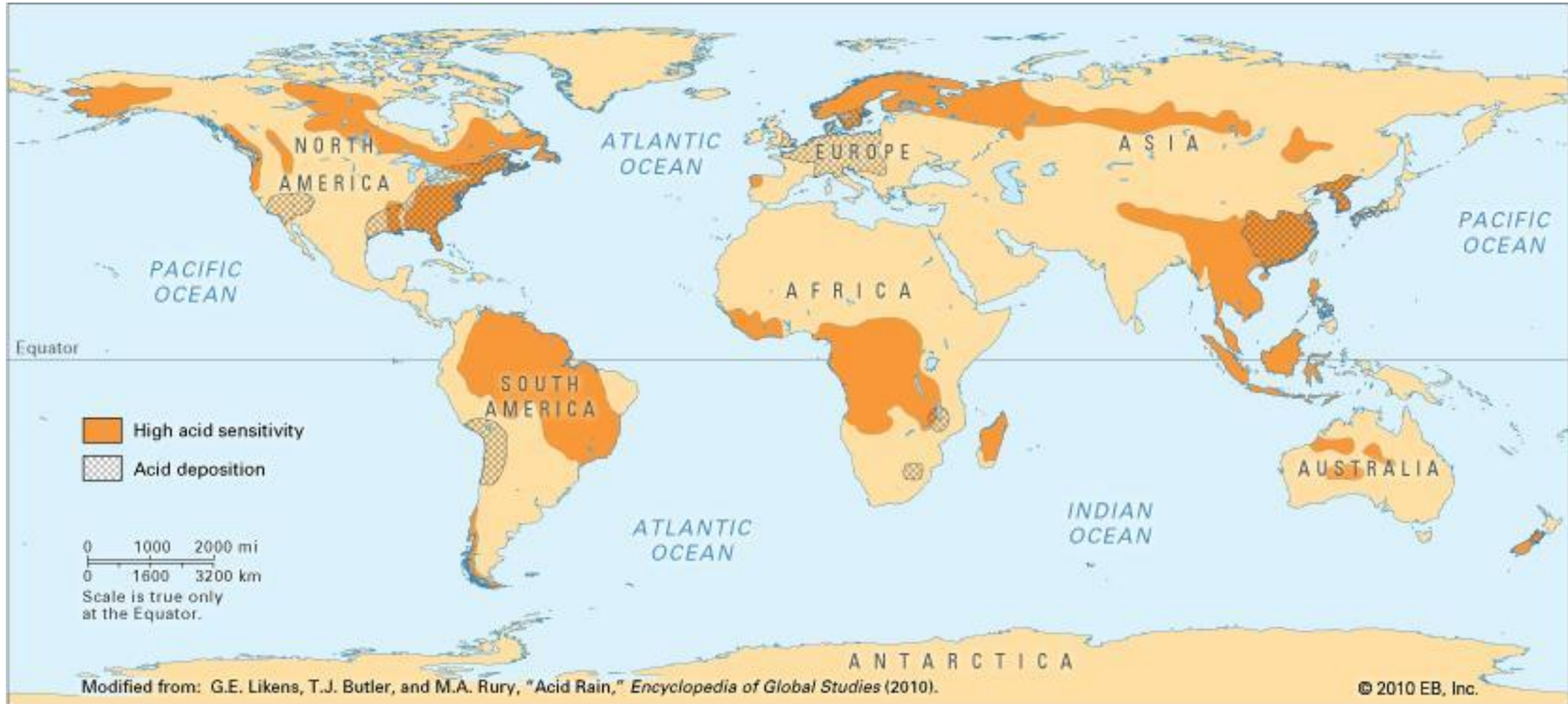
^a distance in meters from the nearest burning shale

^b in mol L⁻¹

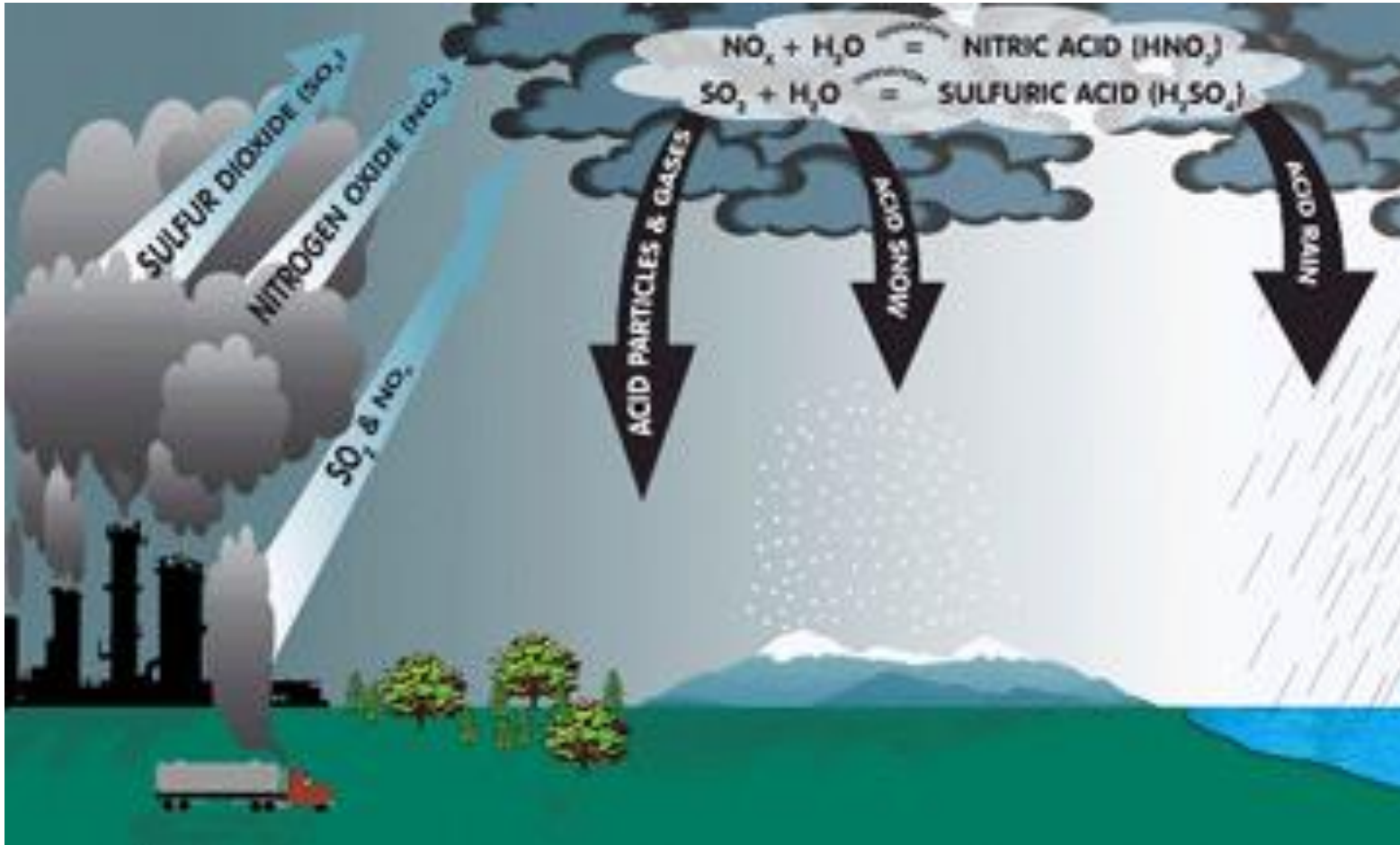
AVERAGE pH OF DEPOSITION



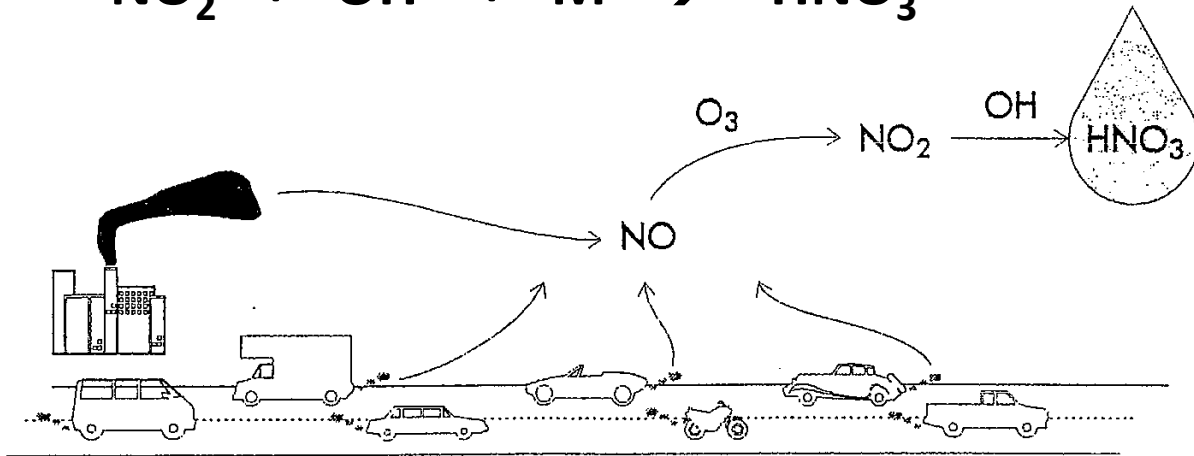
Global distributions of Acid deposition and Acid Sensitivity



4. Mechanisms of HNO_3 and H_2SO_4 production



Atmospheric production and removal of nitric acid



Combustion sources, especially non-point sources, are the principal cause of acid precipitation from nitrogen oxides.

Wet deposition in form of **HNO₃(aq)**

If **NH₃(g)** is present,
→ **NH₄NO₃(aq)**

In dry conditions, **NH₄NO₃(s)**
→ CCN and/or dry deposition

Nitrogen oxides in the atmosphere

Sources:



Natural:

- lightning
- bacteria in soil
- biomass burning



Anthropogenic (man-made):

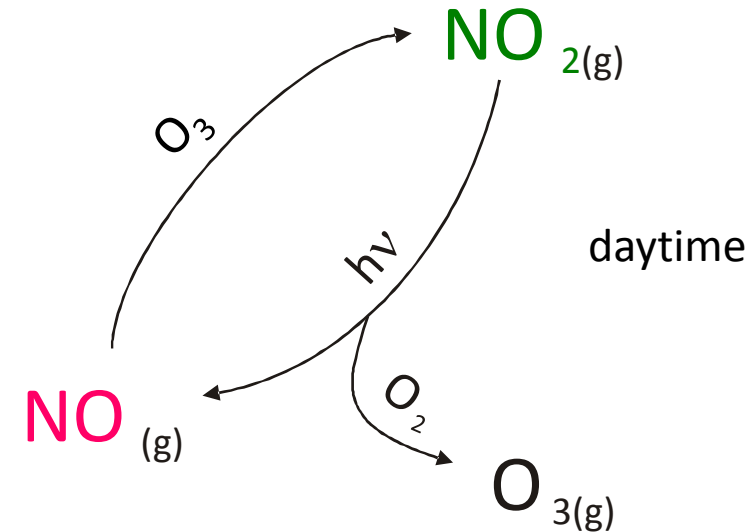
- combustion engines



$\text{NO} \leftrightarrow \text{NO}_2$ interconversion is:

- a chemical null cycle.
- rapid \Rightarrow NO and NO_2 are in steady state.

NO_2 = nitrogen dioxide (brown gas)



NO = nitric oxide
(colorless gas)

Why does NO_x matter?

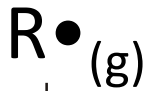


VOC = volatile organic compound

OH = hydroxyl radical = atmospheric oxidant

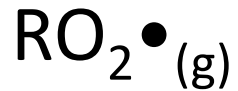


OH



O₂

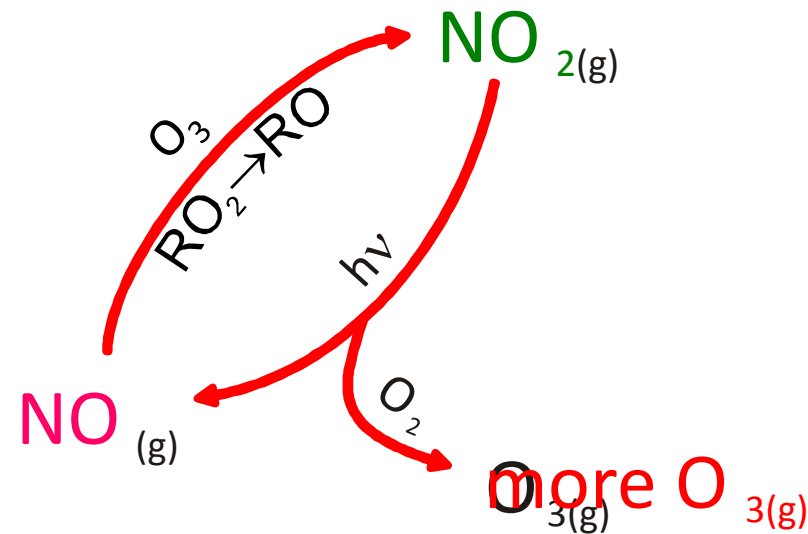
fast



organic peroxy radical

Summary:

- Oxidation of VOCs in the presence of NO_x and sunlight produces O₃.
 - Photochemical O₃ production is catalytic in, and controlled by, NO_x.
 - High [O₃] = increased mortality rates.
- ⇒ atmospheric abundance (sources and sinks) of NO_x is of interest.





NO_x loss: nighttime



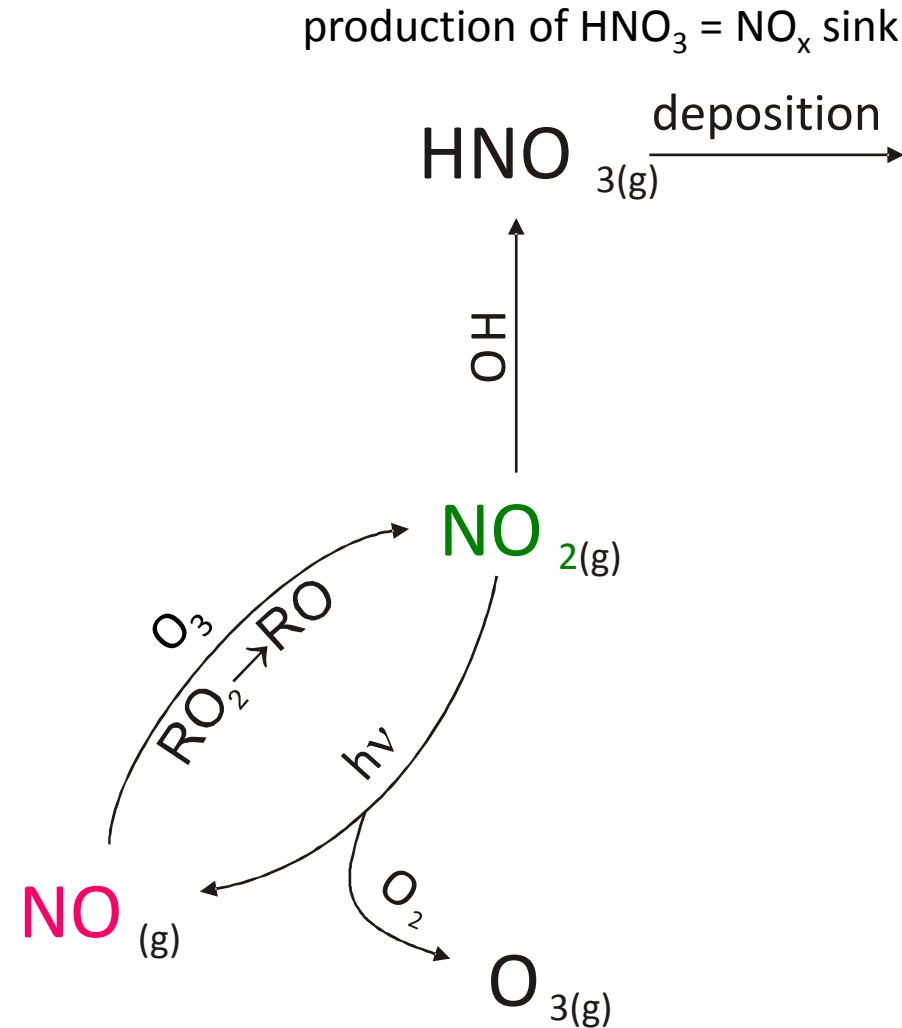
Sources:

Natural:

- lightning
- bacteria in soil
- biomass burning

Anthropogenic (man-made):

- combustion engines





NO_x loss: nighttime

NO₃ = nitrate radical

Sources:

= important oxidant of VOCs

Natural:

N₂O₅ = dinitrogen pentoxide

- lightning (in thermal equilibrium with NO₃)
- bacteria in soil
- = anhydride of nitric acid
- biomass burning

Daytime:

Anthropogenic (man-made):

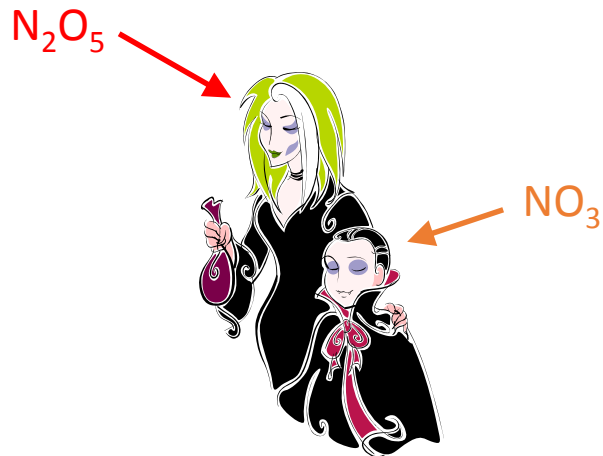
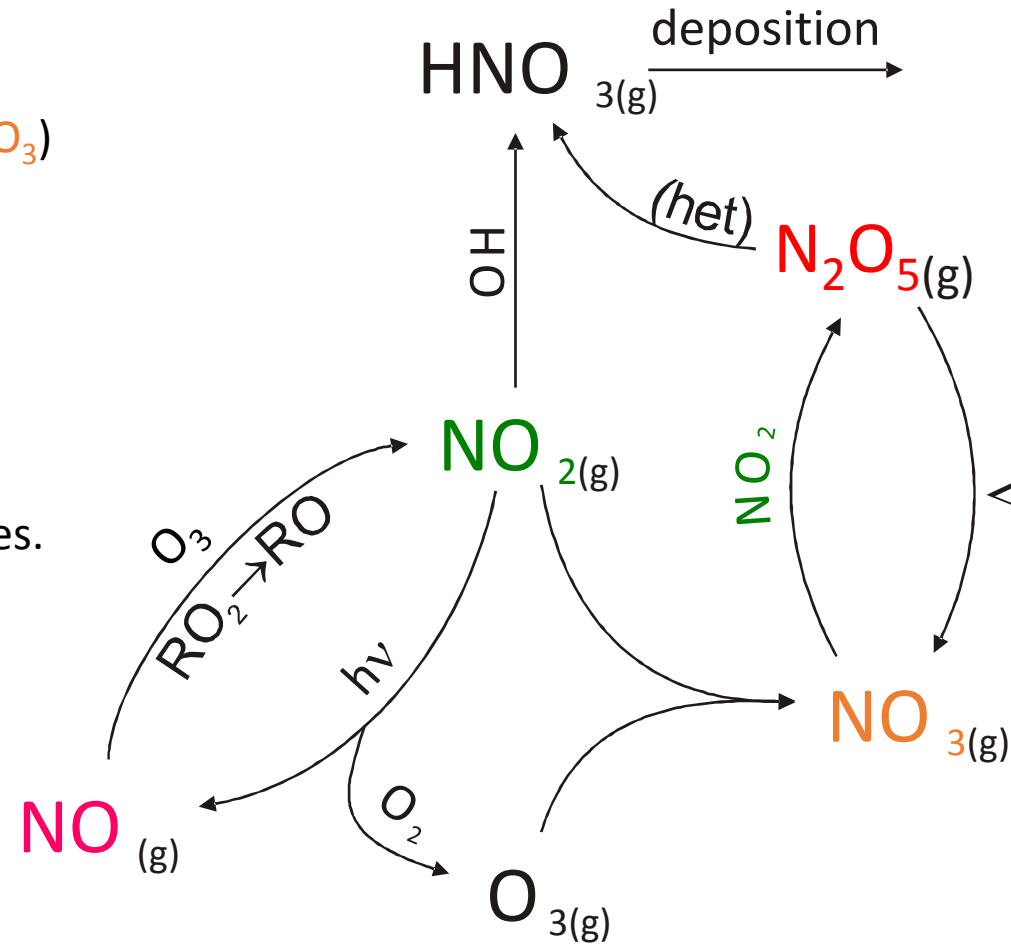


- combustion engines

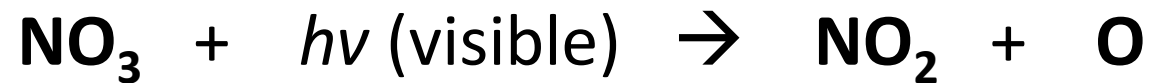


⇒ NO₃ and N₂O₅ are nocturnal species.

production of HNO₃ = NO_x sink

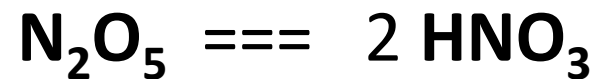
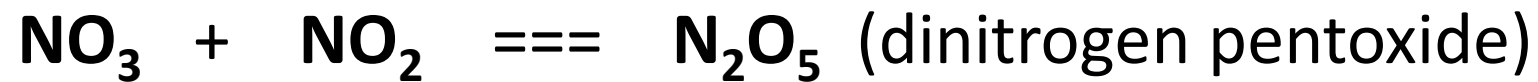


Summary of Night-time NO_2 chemistry



NO_3 accumulates at night

NO_3 reacts like OH (ie H abstraction from R-H and RCHO, addition to alkenes)



Atmospheric production and removal of sulfuric acid

H₂S ($\tau \sim 1-5$ d)

CS₂ ($\tau \sim 40$ d)

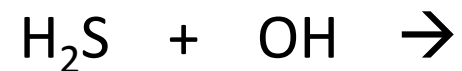
COS ($\tau \sim 1$ yr)

CH₃SH

(CH₃)₂S

CH₃SSCH₃

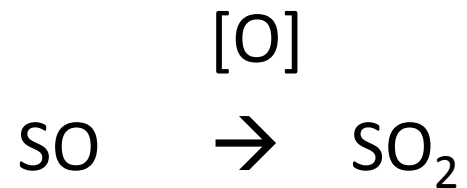
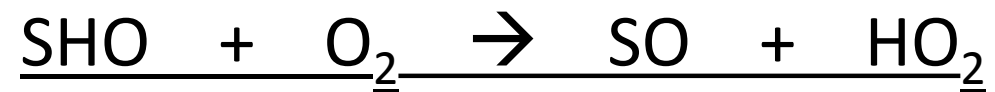
Reaction with **OH** yields **SH** (thionyl radical)



Oxidation of thionyl radical & SO



or



where $[\text{O}] = \text{O}_2, \text{O}_3, \text{NO}_2$

Oxidation of sulfur dioxide (SO₂)

Gas Phase reaction (homogeneous):

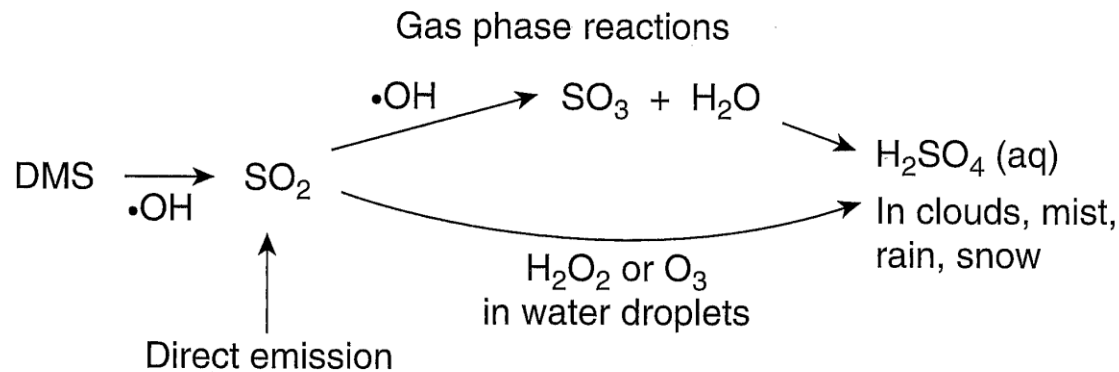
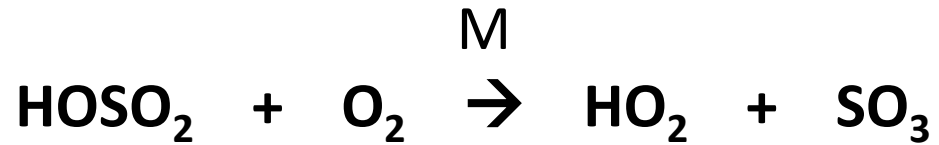
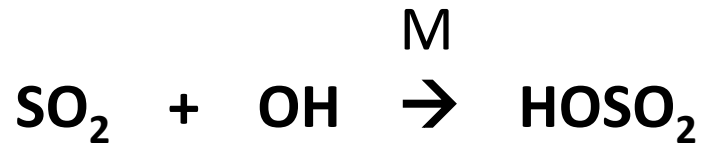
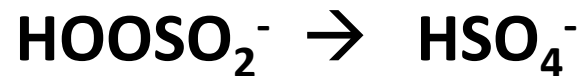
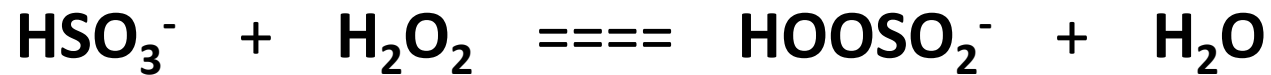
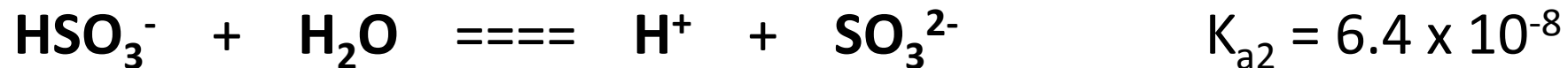


Fig. 5.2 Summary of principal reactions that lead to production of sulphuric acid in atmospheric water droplets.

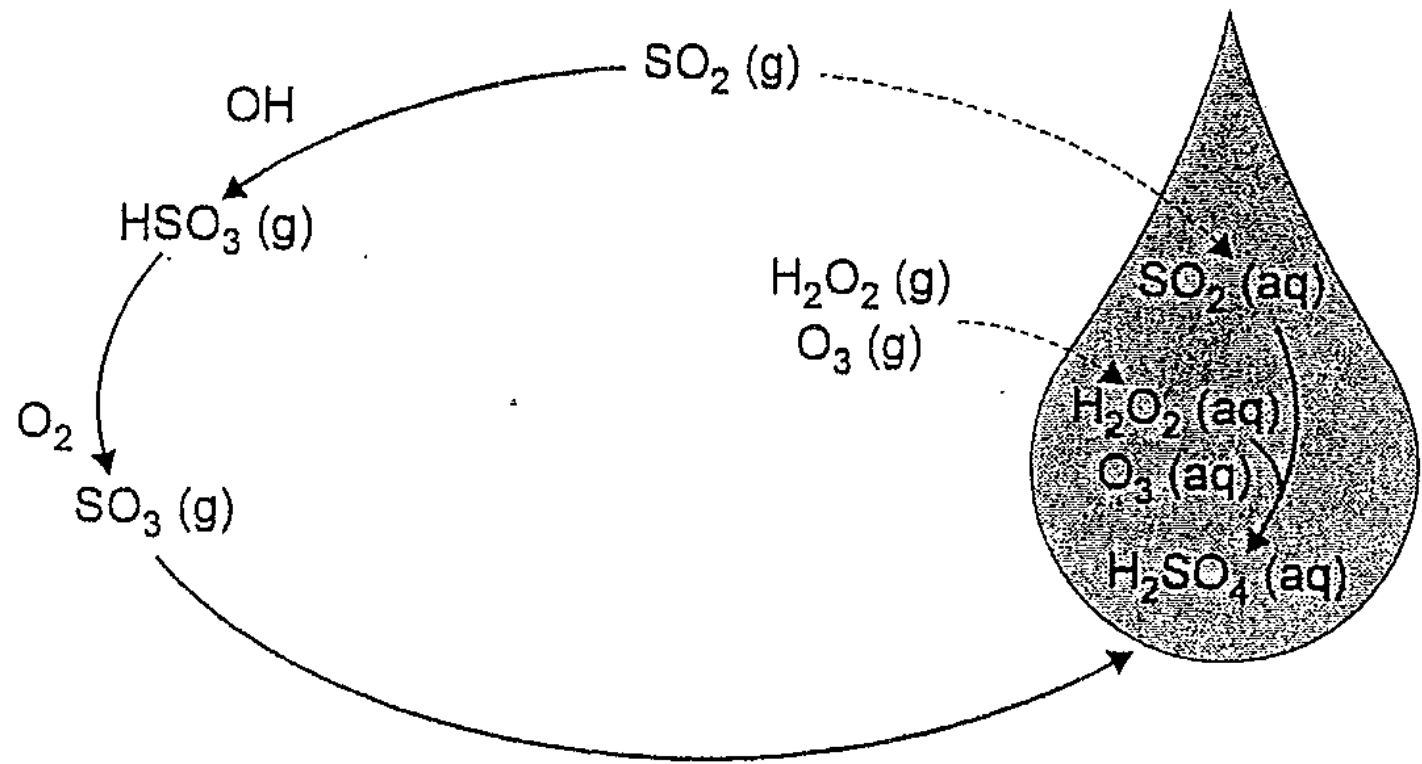
Oxidation of sulfur dioxide (SO₂)

Aqueous phase reaction (heterogeneous):



(H₂O₂ present at 1-2 ppb_v, but K_H is high ~10⁵ M atm⁻¹ or ~ 1 M Pa⁻¹)

H₂O₂ oxidation dominant at pH 2 – 5)



Summary of gas-phase and aqueous-phase oxidation of sulfur dioxide.

Kinetics of SO_2 oxidation

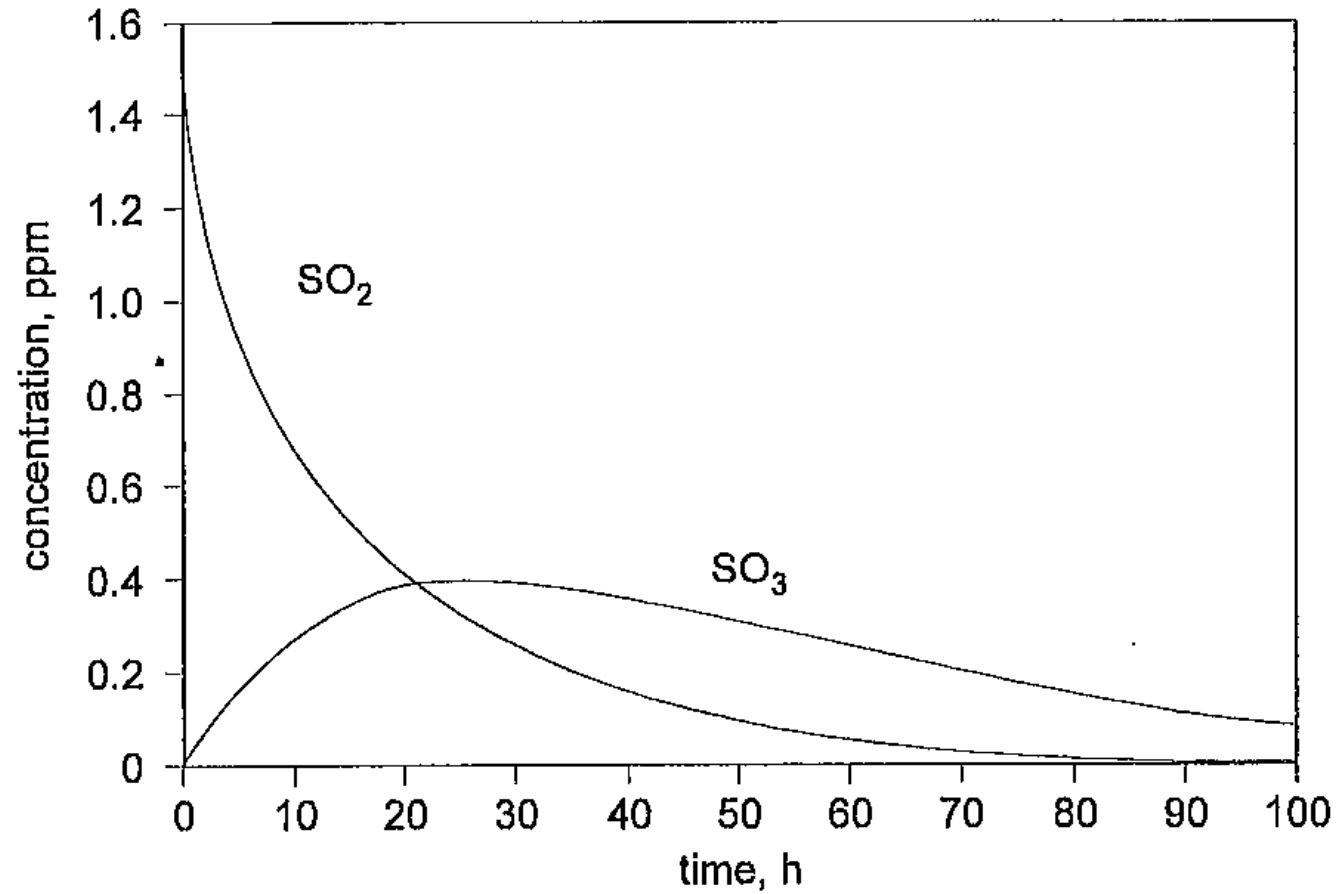


Figure 6.2: Concentrations of $\text{SO}_2(\text{g})$ and $\text{SO}_3(\text{g})$ as a function of the time elapsed since emission.

Carbonyl sulfide (COS) in the stratosphere

Photochemical oxidation leads to $\text{SO}_2 \rightarrow \text{SO}_4^{2-}$ (sulfate aerosols)

Stratospheric aerosols (global cooling effect)

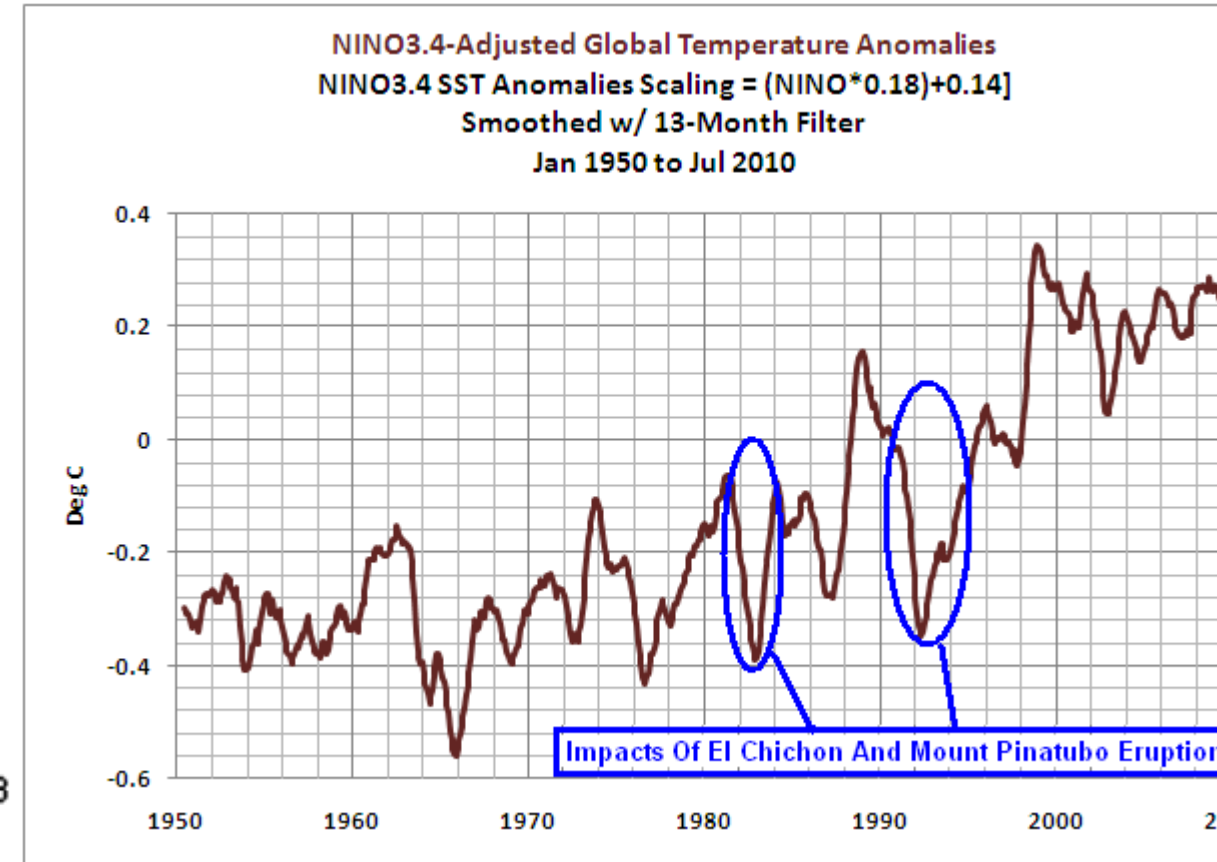
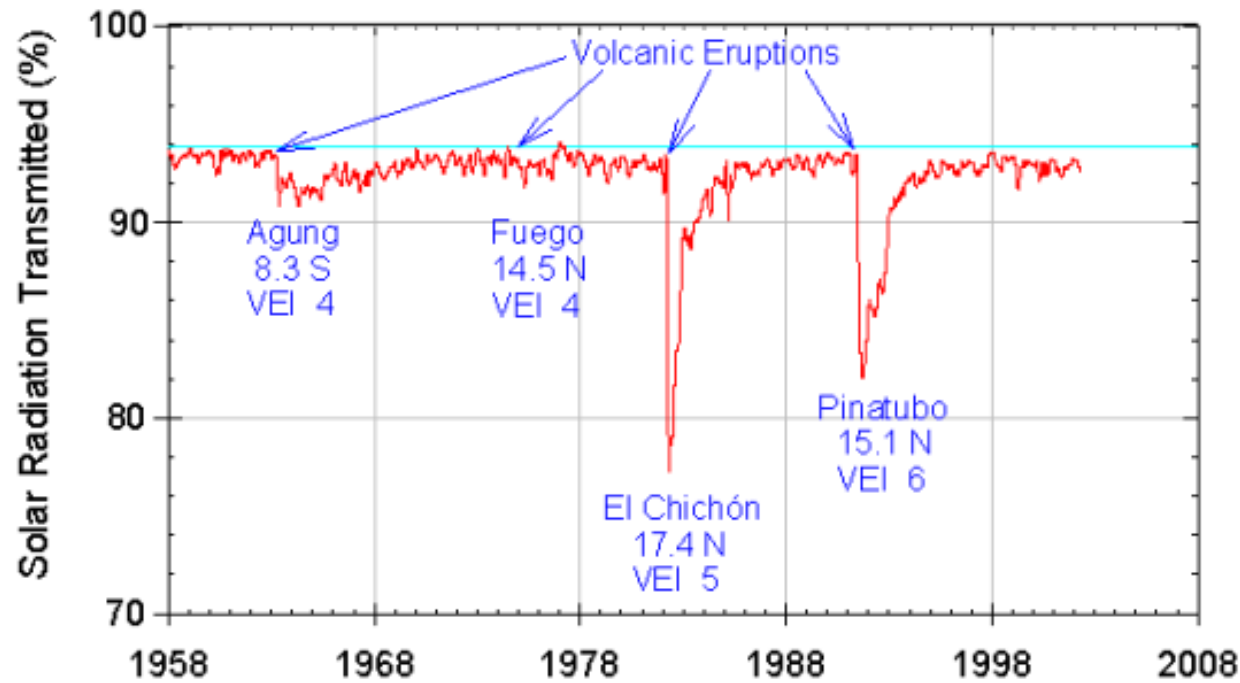
&

Catalytic O_3 loss in polar vortex

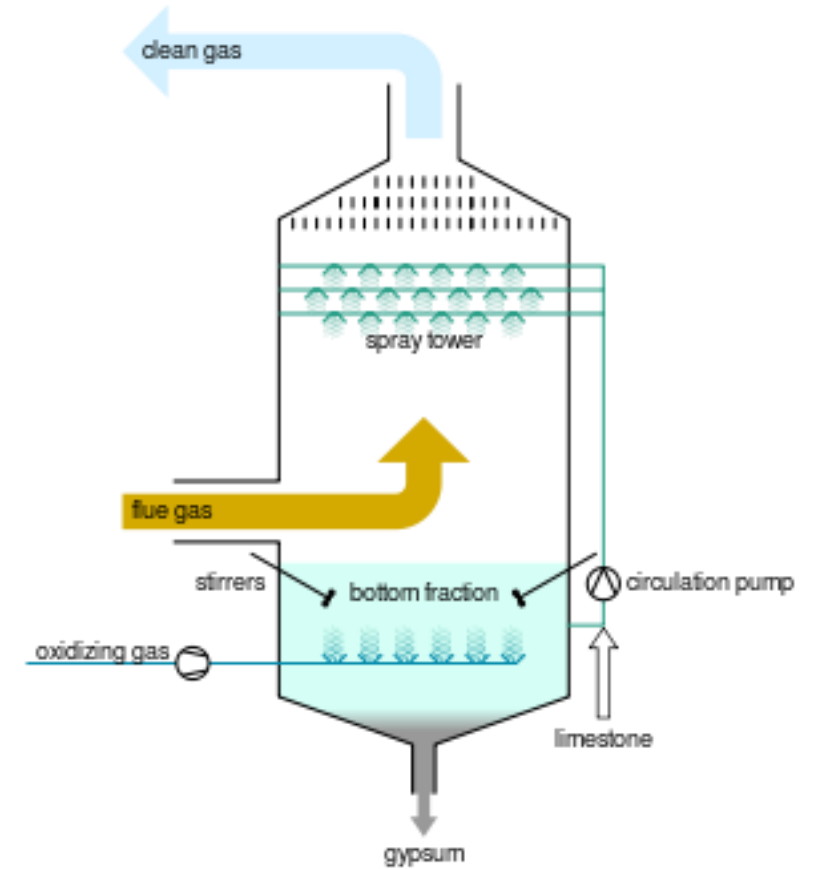
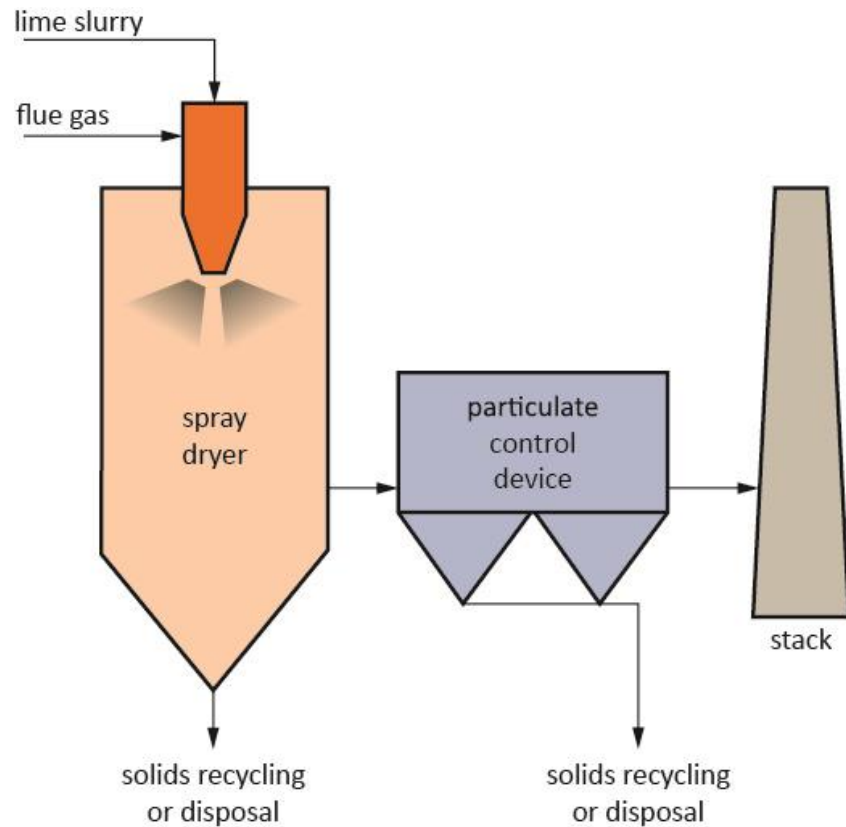


Mt Pinatubo Eruption 1990-91

Mauna Loa Observatory Atmospheric Transmission



5. Emission controls and abatement technology



Fluidized bed combustion

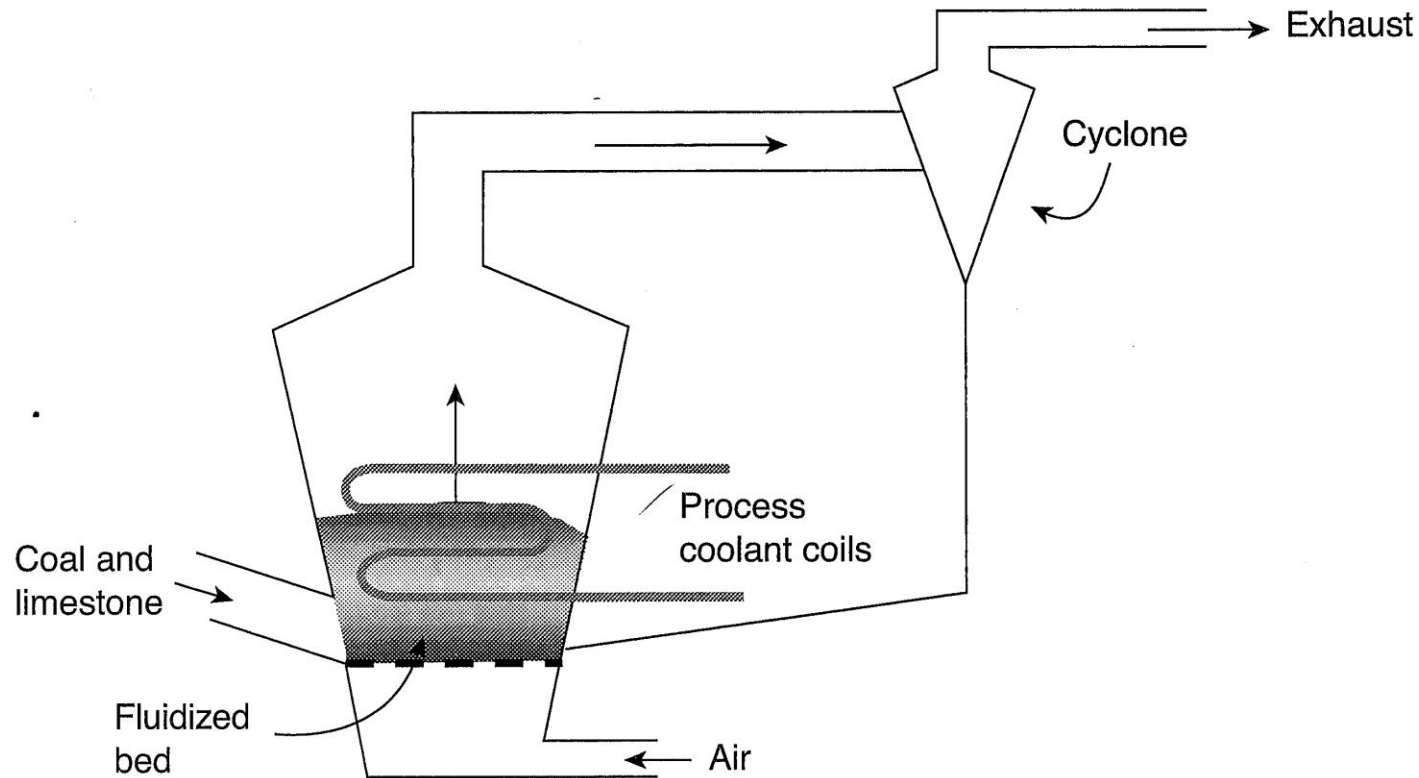
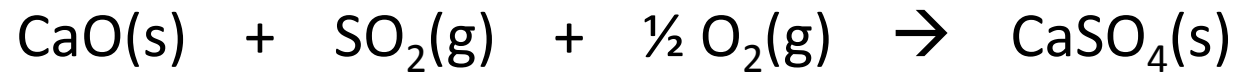
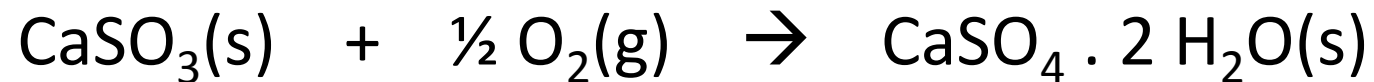


Fig. 5.4 A fluidized-bed combustion unit with cyclone for removal of particulate material in the flue gases.

Flue gas desulphurization



or



SONOX for SO₂ and NO removal

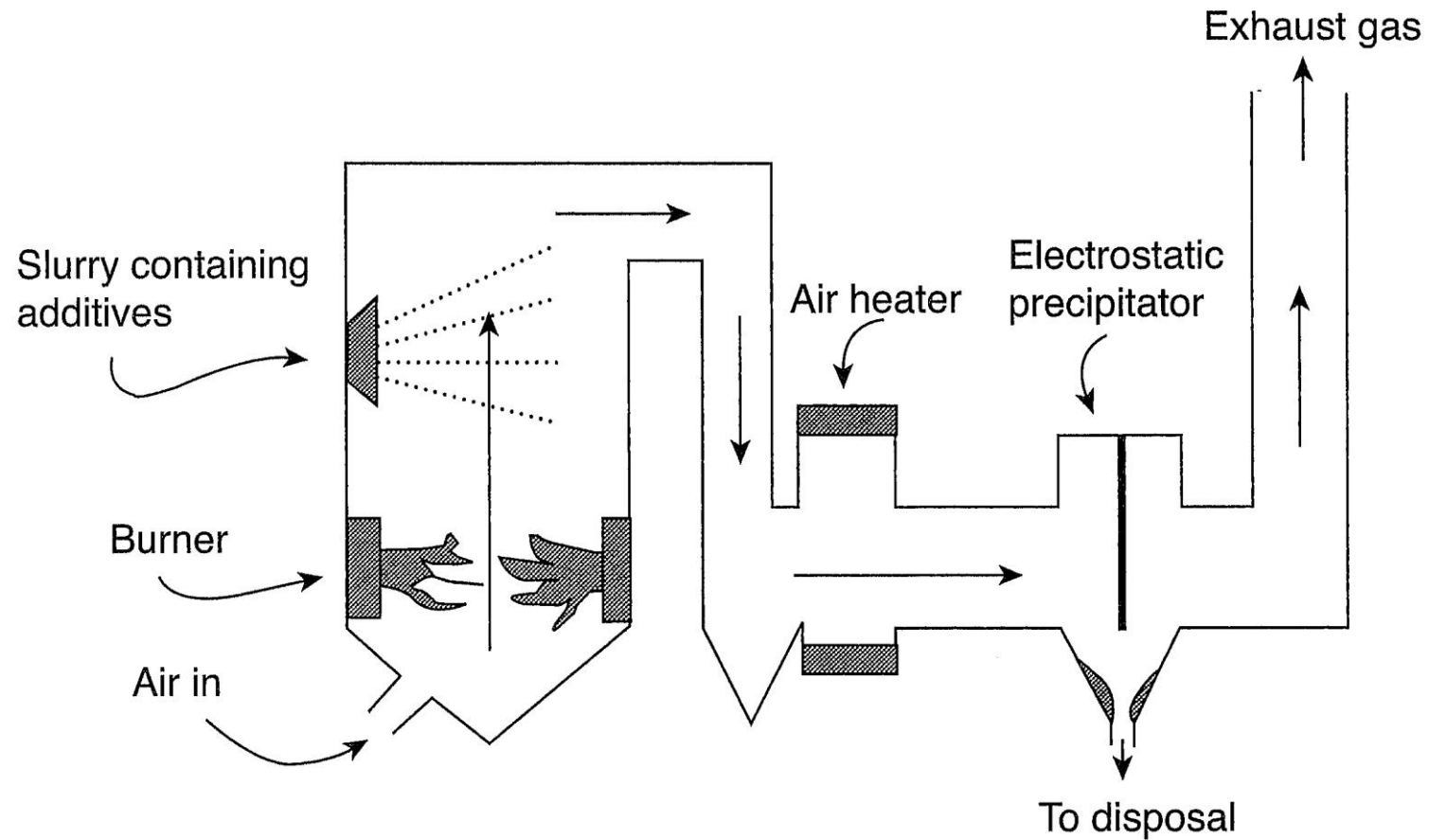
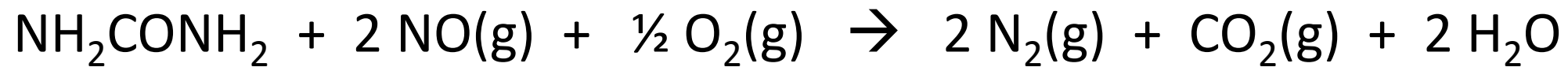
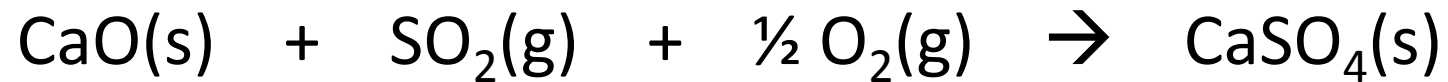
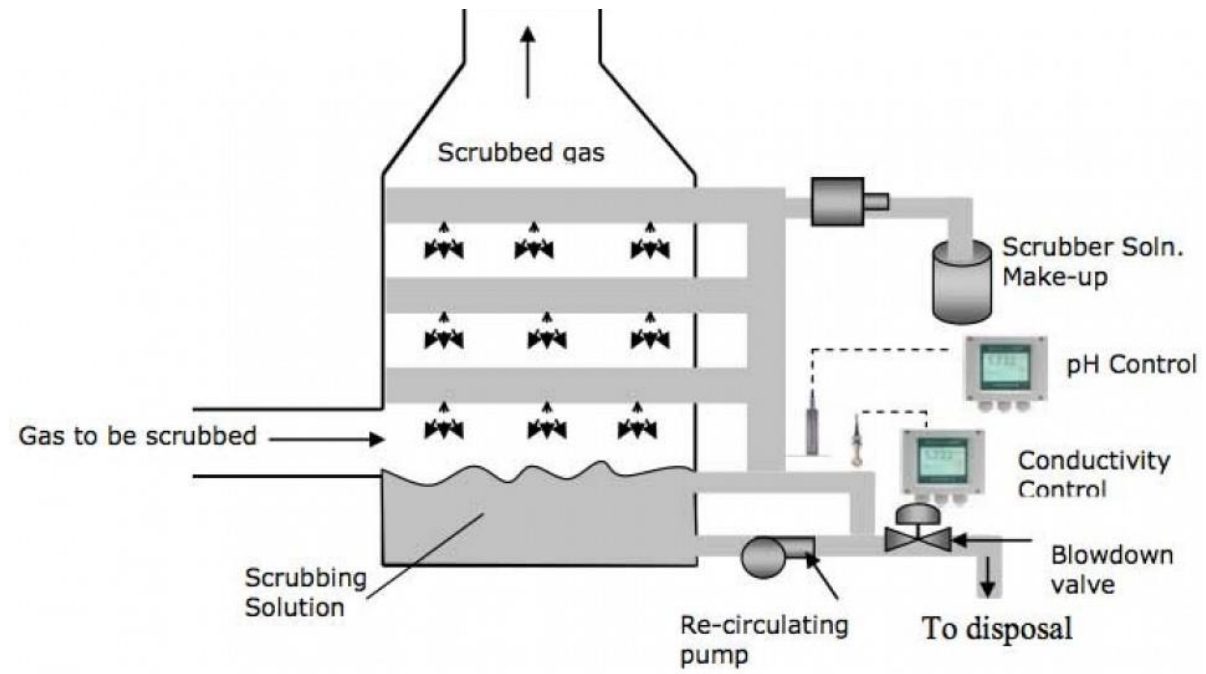


Fig. 5.5 The SONOX process for removal of nitrogen and sulphur oxides from stack gases.

SONOX chemistry





Spray Dryer Absorber (SDA)

