Aqueous Atmospheric Chemistry: Acid Rain (Chapt. 6)

- Review Henry's Law: scavenging of water-soluble gases into clouds, fogs, and rain
- Review normal pH of rainwater ~ 5.6 due to dissolved CO_2
- Acid precipitation a result of industrial activities: emission of SO_2 and NO (H_2S (petrochemical industry) can be oxidised to SO_2)
  also from volcanoes

One major route to NO_x deposition: gas phase oxidation (Chapt. 3)
Photochemical smog chemistry.

$$NO(g) \xrightarrow{O_3 \text{ or } RO_2} NO_2(g) \xrightarrow{OH} HNO_3(g) \longrightarrow HNO_3(aq) \longrightarrow \text{deposition}$$

(OH: sink for NO_2).
(p75, my notes). Also, at night, $NO_3^{\bullet} + RH \rightarrow HNO_3 + R^{\bullet}$ ($NO_2 + O_3 \rightleftharpoons$)

Several routes to SO_2 deposition: gas or aq. phase oxidation (p76, my notes)

High solubility of SO_2 in H_2O:
$$SO_2(g) \xrightarrow{H_2O} H_2SO_3(aq) \longrightarrow \text{deposition}$$
$\rightleftharpoons H^+(aq) + HSO_3^-(aq)$ – see later, p120

Gas phase oxidation:
$$SO_2(g) \xrightarrow{OH} SO_3(g) \xrightarrow{H_2O} H_2SO_4(aq) \longrightarrow \text{deposition}$$
text p165 → (via $HSO_3^{\bullet}$ and oxidn with O_2) – see later p121

Aqueous phase oxidn.:
$$SO_2(g) \xrightarrow{H_2O} H_2SO_3(aq) \xrightarrow{[O]} H_2SO_4(aq) \longrightarrow \text{deposition}$$
$[SO_2(aq)]$; [O] ← by $H_2O_2(aq)$ or $O_3(aq)$ – see later p121

- Acid rain long recognized as a problem; "the" air pollution problem of the '80s, but it is still with us

→ also, heterogeneous oxidn on particles

$$SO_2 + \tfrac{1}{2}O_2 \xrightarrow[\text{catalyst}]{} SO_3 \longrightarrow H_2SO_4(aq) \text{ (or } SO_4^{2-})$$

catalyst ↑ salts of V, Mn, Fe, Cu, Co

} but smaller contribution than other routes (above)

Sources of "acidic gas" emissions

- NO_x all combustion processes, but especially:
  - transportation
  - power generation
  - (metal smelting)

  $N_2(g) \; + \; O_2(g) \; \rightleftharpoons \; 2NO(g)$

- SO_2
  - coal combustion (typically 2-3% sulfur by mass)
  - smelting sulfidic metal ores: many commercially important metals occur as sulfides: Cu, Ni, Pb, Zn

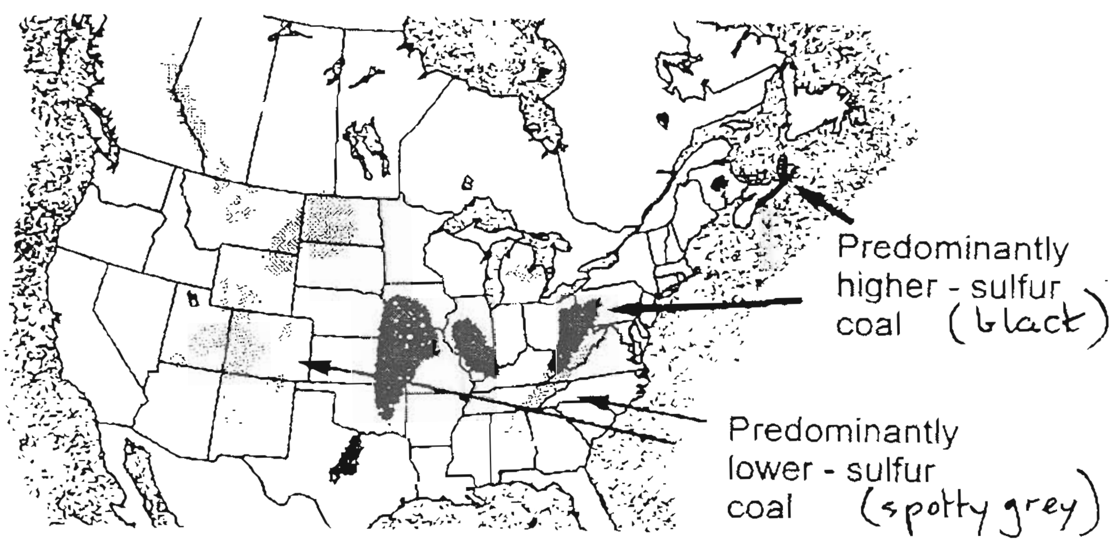
"Roast" in air to give oxide

e.g. $2FeS_2(s) \; + \; 5\frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s) \; + 4SO_2(g)$

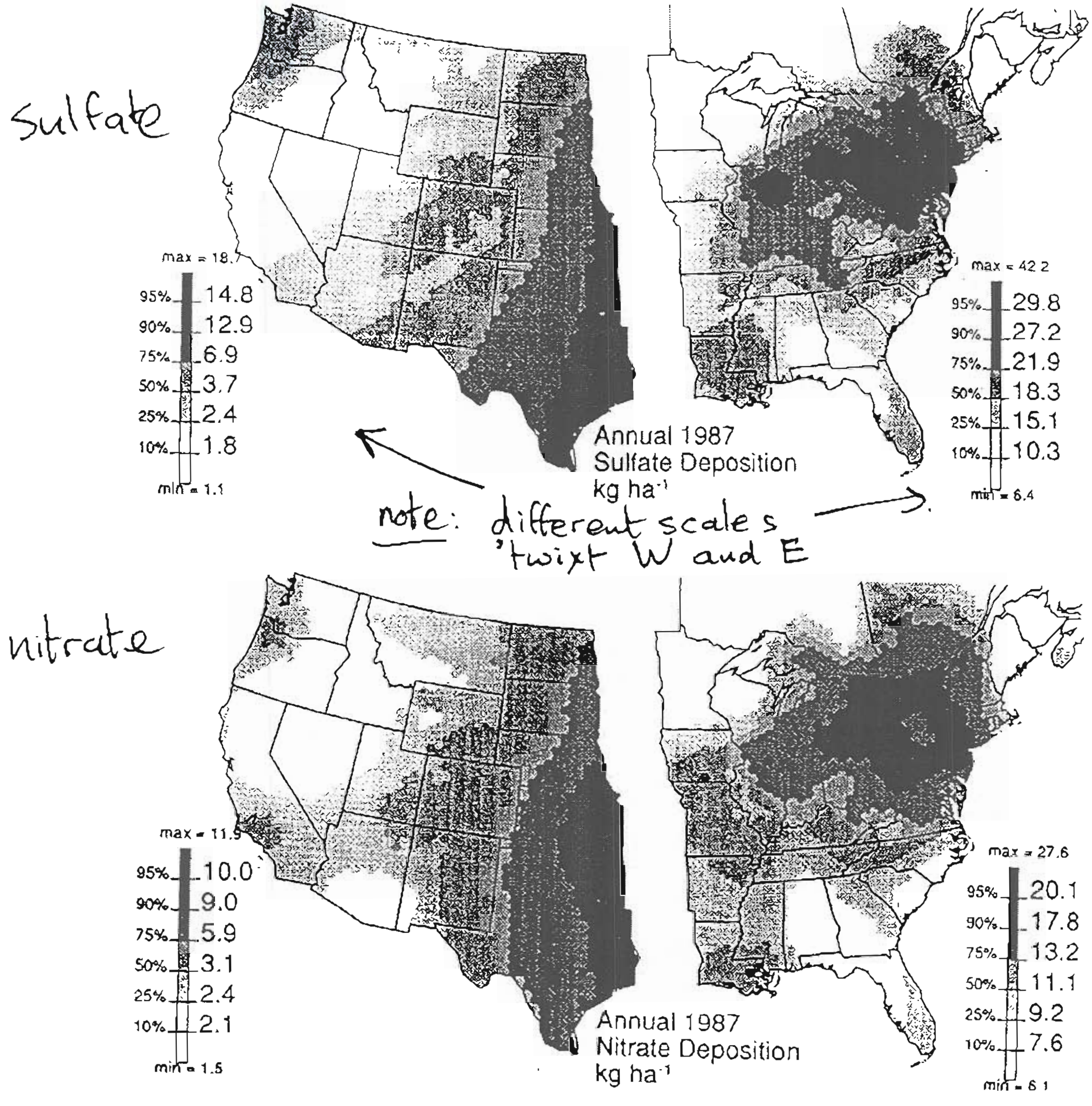
$2NiS(s) \; + \; 3O_2(g) \longrightarrow 2NiO(s) + \; 2SO_2(g)$

Then reduce with coke, e.g. $MO(s) + C(s) \rightarrow M + CO(g)$

ex. p161 text



Acidic Deposition – US Data



- Upper panels sulfate; lower panels nitrate
- Left hand panels scales are ½ those of right hand panels

Importance of aqueous atmospheric chemistry

- High surface to volume ratio of small droplets assures rapid approach to equilibrium: $S/V = 3/r$

$2HO_2 \rightarrow H_2O_2 + O_2 \rightarrow H_2O_2(aq)$. oxidises H_2SO_3 in raindrops etc.

- Removal of soluble species from the gas phase reduces their gas phase concentrations, slowing reaction rates
  - scavenging of HO_2 slows the rate of gas phase oxidation of NO
  - lower concentration of PAN ($CH_3C(O)OONO_2$ (my page 78)) in foggy air because $CH_3CO.OO$ is scavenged into the aqueous phase (i.e. not available for rx. with NO_2).
- Permanent removal if the droplet falls as rain (e.g., HNO_3)

- Possibility of ionic reaction mechanisms in solution (e.g., hydrolysis of N_2O_5 ($+ H_2O \Rightarrow 2HNO_3$); oxidation of SO_2 by H_2O_2: see later) my p 121
- Scattering light by droplets reduces light intensity, especially deep in a cloud, lowers $J(O_3)$ and $J(NO_2)$

Chemistry of Acid Rain

For CO_2:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$K_H = 3.4 \times 10^{-2}$ mol L^{-1} atm^{-1}

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

$K_a = 4.2 \times 10^{-7}$ mol L^{-1}

$$CO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Overall rx.

$K_c = 1.4 \times 10^{-8}$ mol^2 L^{-2} atm^{-1}

For SO_2:

sulphurous acid

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$$

$K_H = 1.2$ mol L^{-1} atm^{-1}

$$H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$$

$K_a = 1.7 \times 10^{-2}$ mol L^{-1}

$$SO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$$

Overall rx.

$K_c = 2.1 \times 10^{-2}$ mol^2 L^{-2} atm^{-1}

- Low (ppbv) concentrations of $SO_2(g)$ change the pH of rainwater more than 375 ppmv of CO_2 because:
  - SO_2 more soluble in water than CO_2 (K_H)
  - H_2SO_3 stronger acid than H_2CO_3 (K_a)

IMP. conclusion

e.g. 0.12 ppmv of $SO_2(g)$ $\Longrightarrow$ pH of 4.3 in H_2O

Compare pH 5.6 from 350 ppmv of $CO_2(g)$

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Oxidation of SO_2

see summary diagram p167 text

Major oxidation route for SO_2 in **dry air**:

$$SO_2(g) \xrightarrow{OH} SO_3(g) \xrightarrow{H_2O} H_2SO_4(aq) \longrightarrow \text{deposition}$$

Details:

$SO_2(g) + OH(g) \longrightarrow HSO_3(g)$ $k = 9\times10^{-13}$ cm^3 molec^{-1} s^{-1}

$HSO_3(g) + O_2(g) \longrightarrow SO_3(g) + HO_2(g)$ ← HO_2 reacts with $NO \rightarrow NO_2 + OH$ i.e. regenerated (catalyst)

Oxidation rate: $k' \sim 10^{-6}$ s^{-1} ⟶ $t_{1/2} \sim 7\times10^5$ s (8 days)

Major oxidation route for SO_2 **when the aqueous phase is present**:

$$SO_2(g) \xrightarrow{H_2O} H_2SO_3(aq) \xrightarrow{[O]} H_2SO_4(aq) \longrightarrow \text{deposition}$$

Details:

$SO_2(g) \longrightarrow H_2SO_3(aq)$

$2HO_2 \longrightarrow H_2O_2 + O_2$ [in gas or aqueous phase]

$H_2SO_3(aq) + H_2O_2 \longrightarrow H_2SO_4(aq) + H_2O$

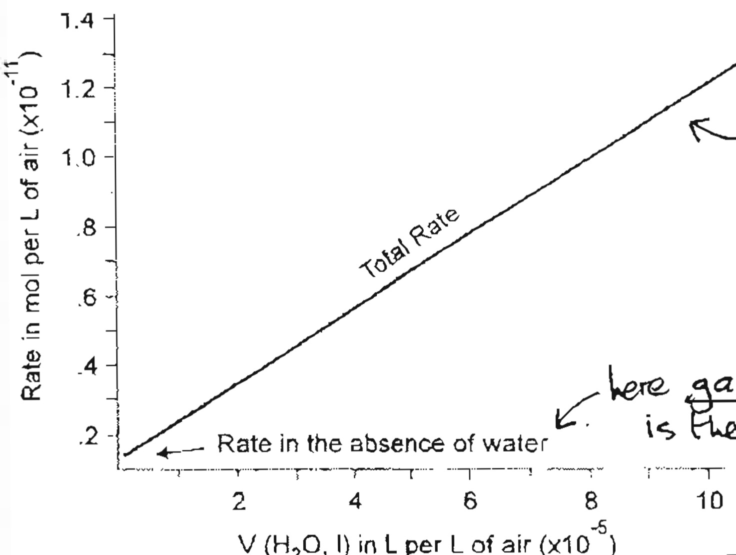
[strongly pH dependent; faster at higher pH]

Aqueous phase oxidation by O_3 is slower

Oxidation rate: up to 10-30% per hour ($t_{1/2} \sim$ 2-7 h); **typical** oxidation rates 0.01-0.1 h^{-1} ($t_{1/2} \sim$ 2-20 h). Thus acid precipitation is a **regional** problem.

not entirely .... in hours → days the air mass can travel beyond national boundaries, e.g. acid rain in Scandinavia can have sources in the UK, France etc. See next page for some distances,

Model for rate as oxidation of SO_2 as a function of volume fraction of water



ex. p 168 in text

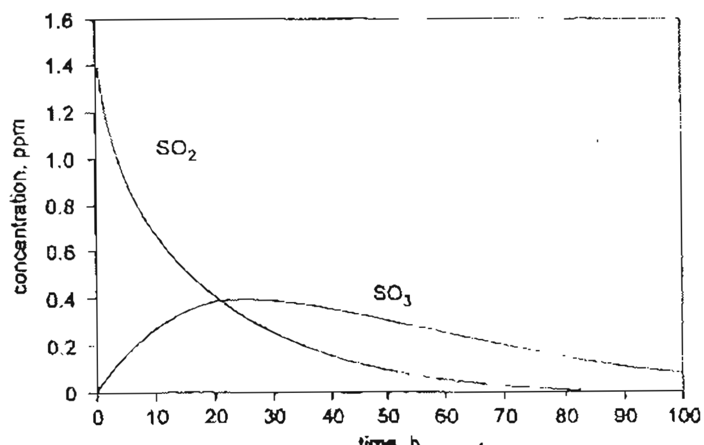
here, wet conditions, rate is fast.

here gas phase oxidn by OH is the main pathway

SO_2 pollution a regional problem

(Compared to CFCs v. long lifetime, distributed globally, migration to stratosphere)

- if $t_{½}$ ~ 2-20 h, and wind speed ~ 20 km/h, then SO_2 pollution is occurring over 40-400 km (one half-life)
- reasonable to assume that SO_2 pollution can extend up to ~ 2000 km



ex p169 text

Concns $SO_2(g)$ and $SO_3(g)$ as function of time elapsed since $SO_2(g)$ emission.

Based on 3 main processes (with reasonable values for rate consts.)

$SO_2 \xrightarrow{k_1} SO_3$

$SO_2 \xrightarrow{k_2}$ deposition as H_2SO_3 (or SO_3^{2-}) sulphite

$SO_3 \xrightarrow{k_3}$ —— " —— H_2SO_4 (or SO_4^{2-}) sulphate

- SO_2 phytotoxic
  - plant growth inhibited at SO_2 concns ~0.1ppmv
  - concns SO_2, 0.1 → 1ppmv cause observable plant injury in a few h.
  - SO_2/NO_2 can act synergistically
  - NO_2 phytotoxic ... but, can form nitrates (plant nutrient)

Effects of acidic emissions

- – effects on plants, on aquatic life, through lowering pH (leaves damaged < pH 3.5; Soil chem. altered > pH 3.5)

  acid rain and forest damage

  Humans: see p173 text ... note.. plants more susceptible
- – susceptible and non-susceptible lakes: $CaCO_3$ as a buffer
  - natural erosion of caves and gorges

$$CaCO_3(s) + H_2CO_3(aq) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$$

$$K = 5.3\times10^{-5}\ (\text{mol L}^{-1})^2 \text{ at } 25^\circ\text{C}$$

  - lakes and streams underlain by $CaCO_3(s)$ have high natural alkalinity. When acidification occurs:
    $HCO_3^-(aq) + H^+(aq) \longrightarrow H_2CO_3(aq) \longrightarrow CO_2(g)$
    the $HCO_3^-(aq)$ consumed is replaced by dissolution of more $CaCO_3$ (→ HCO_3^-)
    (i.e. lakes in limestone areas are insensitive to acidification)

    see etching of stonework p175 text.
  - effects on structures, especially limestone and steel
    Net reaction for limestone can be written as: (sum)

$$CaCO_3(s) + H^+(aq) \rightleftharpoons Ca^{2+}(aq) + HCO_3^-(aq)$$

$$K = 1.3\times10^{+2}\ \text{mol L}^{-1} \text{ at } 25^\circ\text{C}$$

  - in the case of sulfur oxide emissions, "sulfation" leads to flaking off from the surface (See Fig p175)

$$CaCO_3(s) + \tfrac{1}{2}O_2(g) + SO_2(g) \longrightarrow CaSO_4(s)$$

  - Read for yourselves text pp. 176-182: natural waters and aluminum solubility

→ discusses lakes in granitic areas (not buffered, unlike limestone areas, above)
pH often < 5.0

e.g. (see p177 text) pH 4.5, death of eel and brook trout.
Many fish, perch, pike, salmon, rainbow trout die around pH 5 → 5.5

Acidification of lake waters ⇒ dissolution of metal ions including Cd^{2+}, Pb^{2+}, Hg^{2+} ⇐ nasty
Al^{3+}

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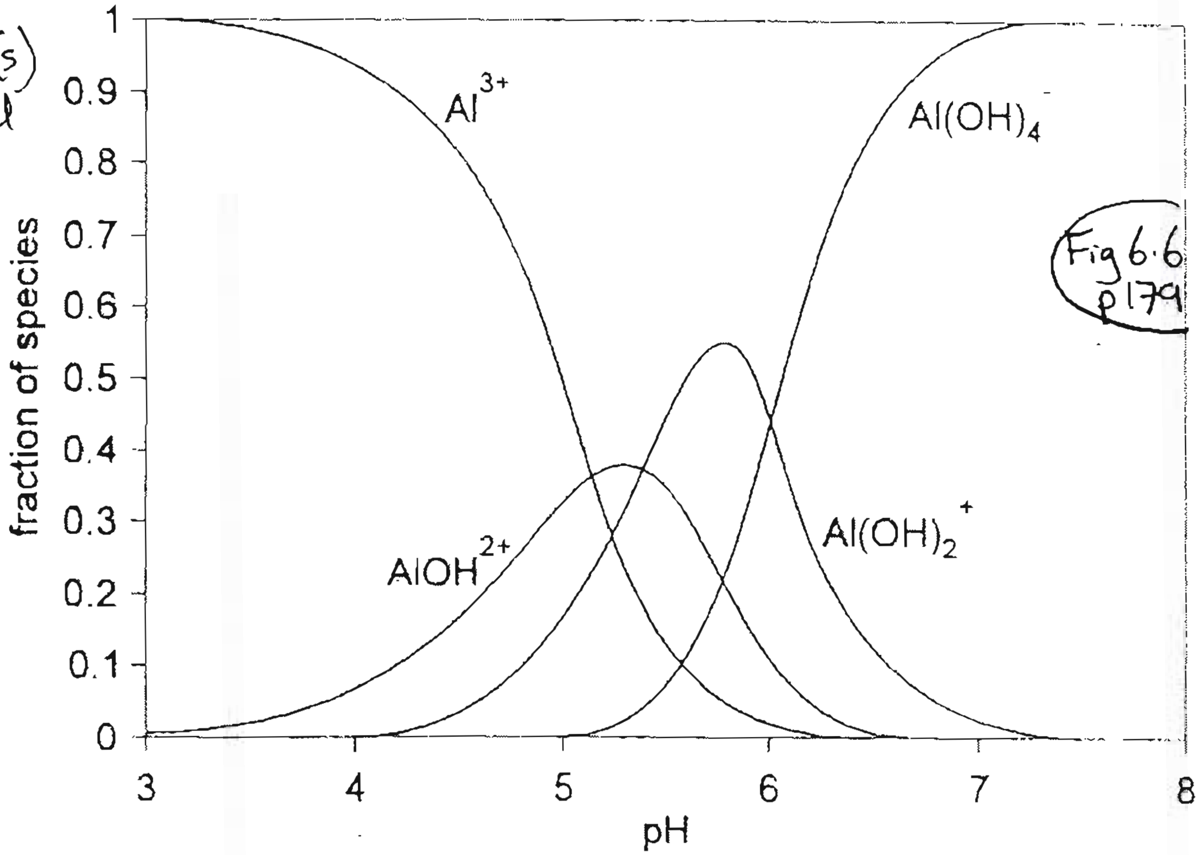
i ← grrr!!

Aluminum solubility (aluminium highly toxic to fish)

- aluminum speciation: solubility minimum near pH 6.5 (see Fig 6.7)

From $Al_2O_3(s)$ hydrated



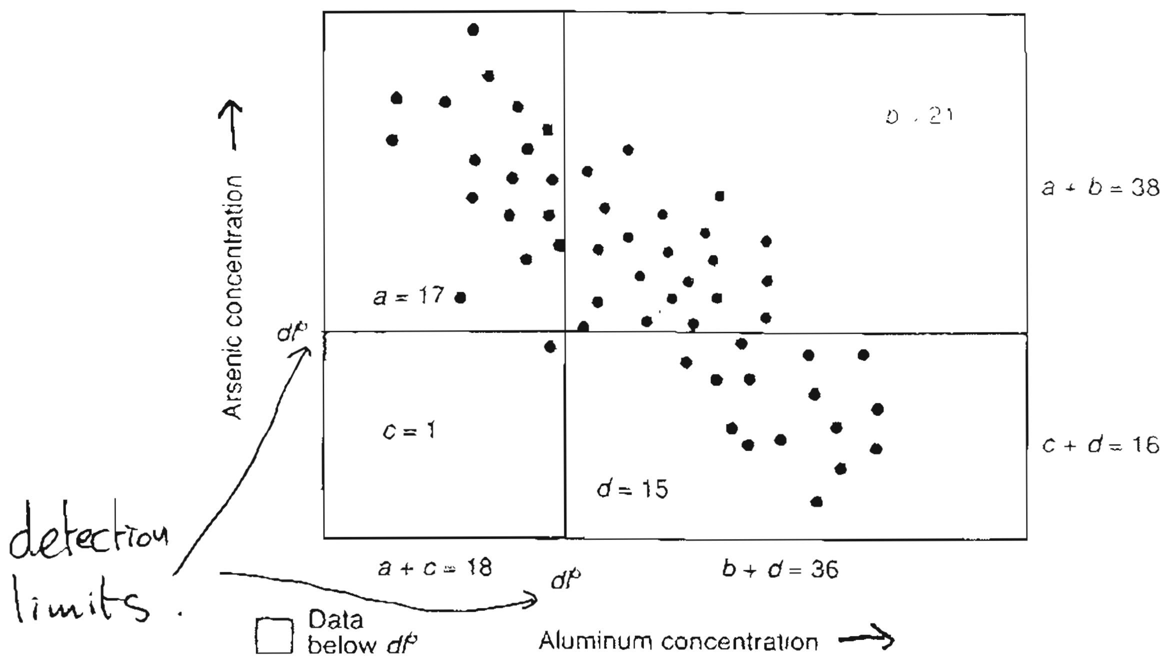
$$Al^{3+}(aq) \rightleftharpoons AlOH^{2+}(aq) \rightleftharpoons Al(OH)_2^+(aq) \rightleftharpoons Al(OH)_3(s) \rightleftharpoons Al(OH)_4^-(aq)$$

- Fluoride raises the overall solubility of aluminum: relevant to aluminum smelters which tend to release HF

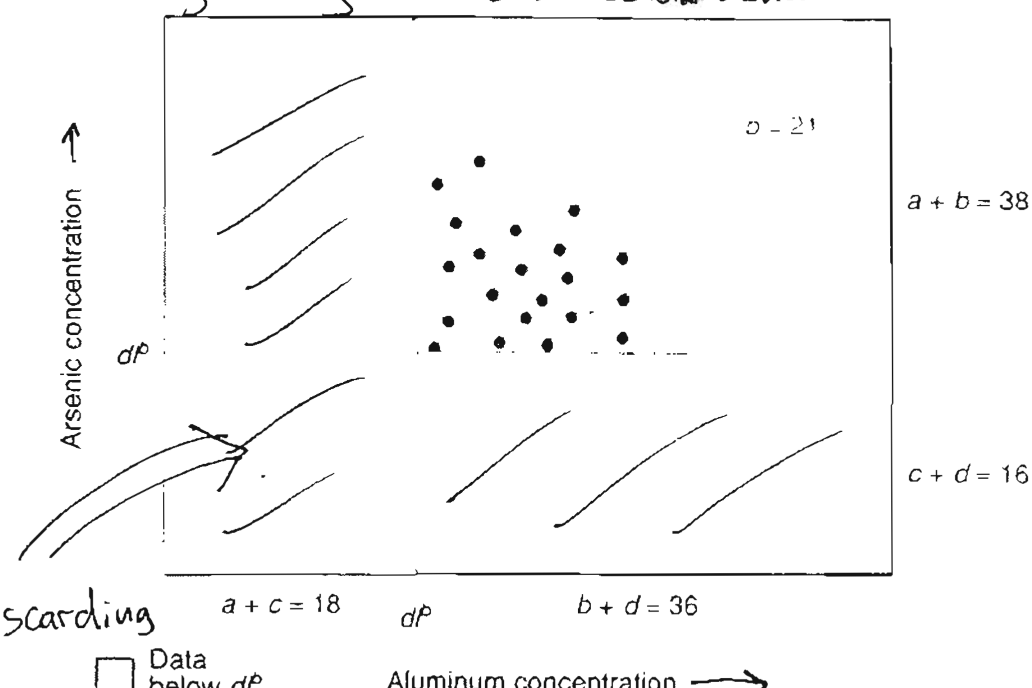
$$Al^{3+}(aq) \rightleftharpoons AlF^{2+}(aq) \rightleftharpoons AlF_2^+(aq)$$

- Arsenic lowers the concentration of dissolved aluminum: *Environ. Sci. Technol.* 1990, p. 1774

$$Al^{3+}(aq) + AsO_4^{3-} \rightleftharpoons AlAsO_4(s) \qquad \text{[oversimplified!]}$$



Ignoring the "censored data"



by discarding the "less thans" (known as "censored data"). i.e. data below the detection limits (dl), the relationship between [Al] and [As] is lost.

Abatement of acidic emissions

NO$_x$ New technology involving ammonia injection into the exhaust gas stream:

$$NO_x + NH_3 \longrightarrow N_2 + H_2O \quad \text{(not balanced)}$$

- Proposed use at Southdown gas-fired generating station in Mississauga; question of whether highly polluting Lakeview and Nanticoke stations should be decommissioned
- Particularly useful for gas-fired plants where there is no SO_2 in the flue gases

SO_2 from coal combustion

Combustion of 1 tonne of coal that is 2% sulfur by mass —>

- 80,000 mol CO_2
- 320,000 mol N_2
- 600 mol of SO_2 (~0.15% of the total: uneconomic to recover) .. in the past abatement was simply dilution (i.e. build a tall stack to disperse the gases) e.g. INCO stack, Sudbury area ... just sends problem elsewhere)

Flue Gas Desulfurization (FGD) technology to remove SO_2 by passing a slurry of ground lime or limestone down the stack as the hot flue gases pass upwards

$$SO_2 + Ca(OH)_2 \longrightarrow CaSO_3 + H_2O$$

also $$SO_2 + Ca(OH)_2 + \tfrac{1}{2}O_2 \longrightarrow CaSO_4 + H_2O$$

$$SO_2 + CaCO_3 \longrightarrow CaSO_3 + CO_2$$

Improved combustion methods

- coal cleaning: separate finely divided coal particles by froth flotation, since coal has d = 2.3 g cm^{-3} while pyrite FeS_2, the main sulfur species has d = 4.5 g cm^{-3}

- fluidized bed combustion: mix finely ground coal with limestone and burn the fine particles on a screen so that the particles are supported by the combustion air train. Sulfur in the coal —> $CaSO_3/CaSO_4$ ← but difficult to dispose.

SO_2 from metal refining

- Problem is sulfide ores

  e.g. $2FeS_2(s) + 5\frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s) + 4SO_2(g)$

  $2NiS(s) + 3O_2(g) \longrightarrow 2NiO + 2SO_2(g)$

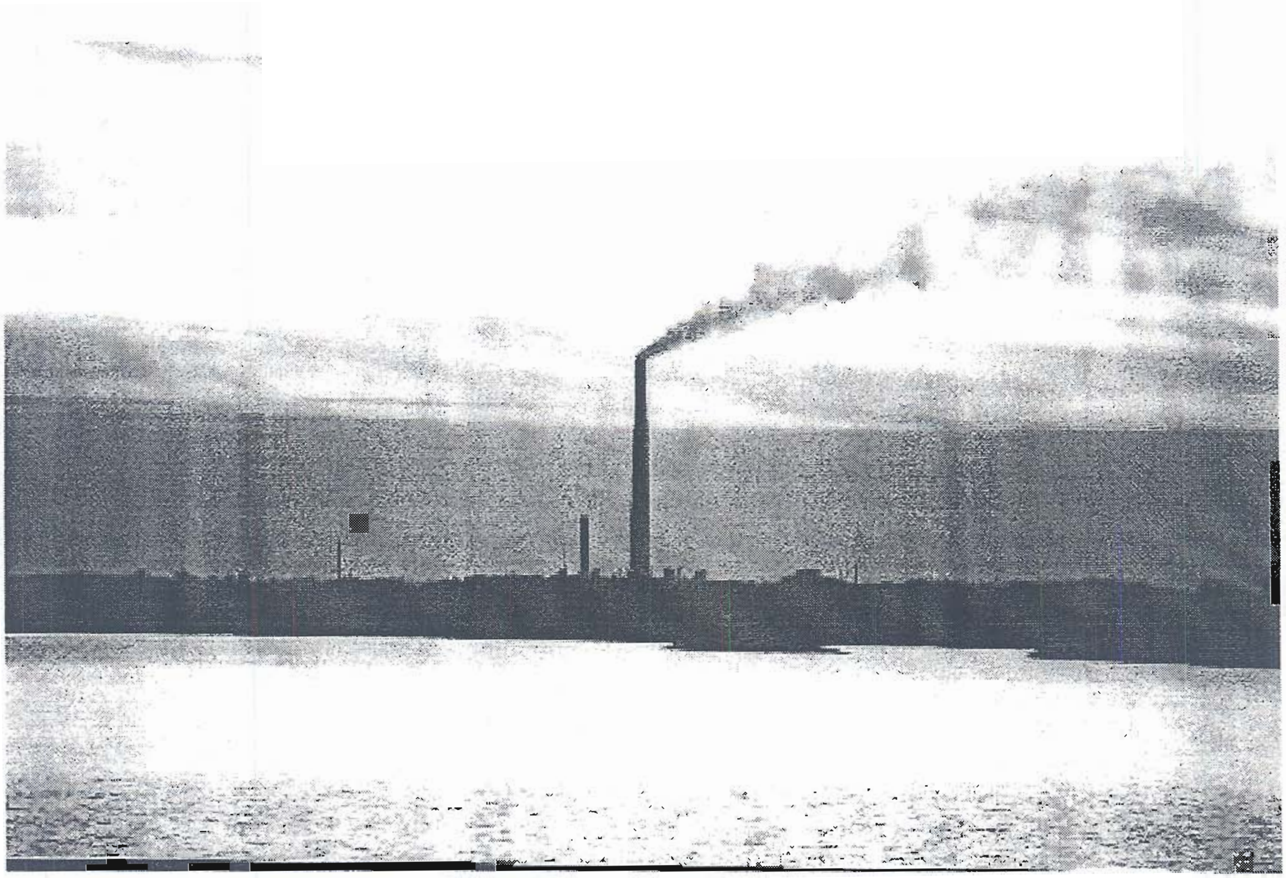
Unlike coal combustion, there is enough SO_2 to collect as $SO_2(l)$ or to convert into H_2SO_4. Unfortunately, both these are very cheap commodity chemicals; H_2SO_4 by this route must compete with purer material from virgin sulfur or natural gas "sweetening" (catalytic oxidation of H_2S to elemental S)

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g) \quad [V_2O_5 \text{ catalyst, } 450^\circ C]$$

$$SO_3(g) + H_2SO_4(l) \longrightarrow \underset{\text{oleum}}{H_2SO_4.SO_3(l)} \xrightarrow{H_2O} H_2SO_4(\text{conc.})$$

INCO (Sudbury) has reduced SO_2 emissions by 95% since the 1970s

The INCO Superstack (photo from
http://www.geocities.com/Pentagon/5094/inco.jpg



The stack, erected 1970-1972, is 400 m high and is the tallest free standing stack in the world ... an example of "dilution is the solution to pollution", I'm afraid!!

Land reclamation at the INCO site: Dan Shaw,
http://www.hort.agri.umn.edu/h5015/99papers/shaw.htm