

## Water and Dissolved Chemicals

- Recall Henry's Law, solubility of gases in water, describes partitioning (depends on how you look at it)
  - Water from air
  - Air from water
    - In first case, mass loading of water with airborne chemicals, treating water as a sink
      - CO<sub>2</sub> in the atmosphere dissolving in seawater
- Be sure to understand the units to decide if looking at Water from air or air from water.
- Be sure to also understand if dissolved chemical is a gas, such as CO<sub>2</sub>, or an organic chemical.
  - Gases are more soluble with decreasing water temperature, while simultaneously organic chemicals are less soluble
- In the simplest of cases, the dissolved chemical is assumed not to ionize in solution upon dissolution.
- Units (remember, these are T dependent):
  1.  $K_H (\text{mol L}^{-1} \text{ atm}^{-1}) = C_X/P_X$ , or
  2.  $K_H (\text{Pa m}^3 \text{ mol}^{-1}) = P^*/C_{W(\text{max})}$ 
    - For 1, a large  $K_H$  means high solubility;  $K_H$  always decreases with T; gases less soluble at higher T (all gases, all solvents)

- Henry's law constants at 298 K:
  - Seinfeld and Pandis, Atmospheric Chemistry and Physics, Wiley, 1998 p. 341
- Some  $K_H$  constants,  $\text{mol L}^{-1} \text{atm}^{-1}$ 
  - $\text{O}_2$  .....  $1.3 \times 10^{-3}$
  - $\text{NO}$  .....  $1.9 \times 10^{-3}$
  - $\text{NO}_2$  .....  $1.2 \times 10^{-2}$
  - $\text{O}_3$  .....  $1.13 \times 10^{-2}$
  - $\text{N}_2\text{O}$  .....  $2.5 \times 10^{-2}$
  - $\text{CO}_2$  .....  $3.4 \times 10^{-2}$
  - $\text{H}_2\text{S}$  ..... 0.12
  - $\text{SO}_2$  ..... 1.23
  - $\text{CH}_3\text{ONO}_2$  ..... 2.6
  - $\text{CH}_3\text{O}_2$  ..... 6
  - $\text{OH}$  ..... 25
  - $\text{HNO}_2$  ..... 49
  - $\text{NH}_3$  ..... 62
  - $\text{CH}_3\text{OH}$  ..... 220
  - $\text{CH}_3\text{OOH}$  ..... 230
  - $\text{HCl}$  ..... 730
  - $\text{HO}_2$  ..... 2000
  - $\text{CH}_3\text{COOH}$  ..... 8800
  - $\text{H}_2\text{O}_2$  ..... 75,000
  - $\text{HNO}_3$  ..... 200,000

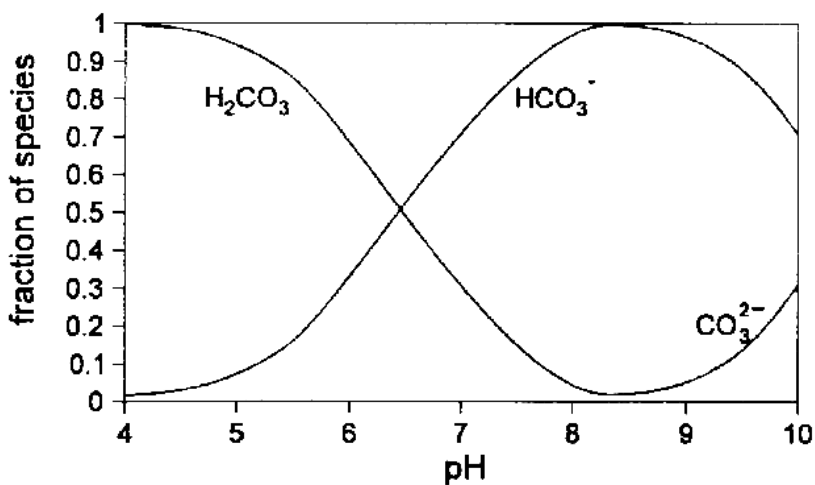
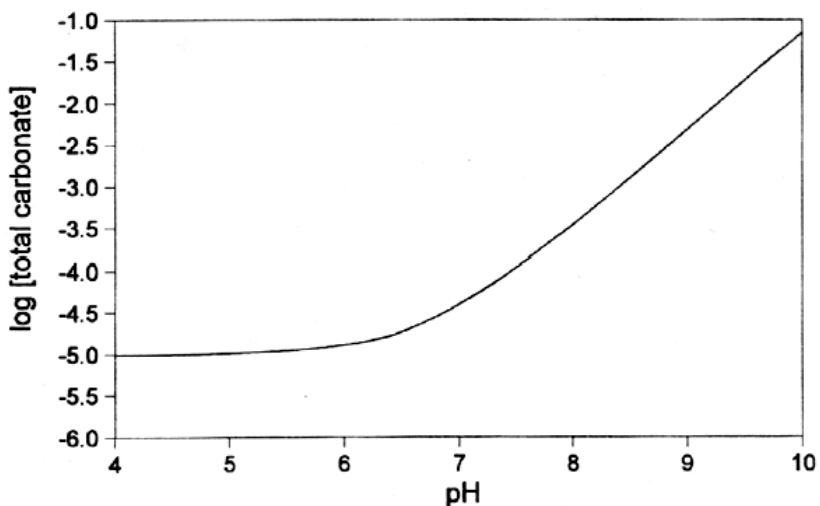
## ***Basic Tests***

- Biological Oxygen Demand (BOD)
  - Incubate with microorganisms for 5 days in closed container, measure  $c(\text{O}_2)$  before and after
- Chemical Oxygen Demand (COD)
  - Titrate the sample against excess  $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}^+$
  - Easily oxidized substances consume  $\text{Na}_2\text{Cr}_2\text{O}_7$ ; determine the amount of  $\text{Na}_2\text{Cr}_2\text{O}_7$  left over
    - 1 mol  $\text{Na}_2\text{Cr}_2\text{O}_7/$  1.5 mol  $\text{O}_2$
- Total Organic Carbon (TOC)
  - oxidize the organic compounds to  $\text{CO}_2$  by combustion; analyze  $\text{CO}_2$  produced
- Dissolved Oxygen (DO)
  - done by titration:  
$$\text{Mn}^{2+} + 2\text{OH}^- + \frac{1}{2}\text{O}_2 \rightarrow \text{MnO}_2(\text{s}) + \text{H}_2\text{O}$$
$$\text{MnO}_2 + 4\text{H}^+ + 2\text{I}^- \rightarrow \text{I}_2 + \text{Mn}^{2+} + 2\text{H}_2\text{O}$$
$$\text{I}_2 + \text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$$

## CO<sub>2</sub> solubility in water

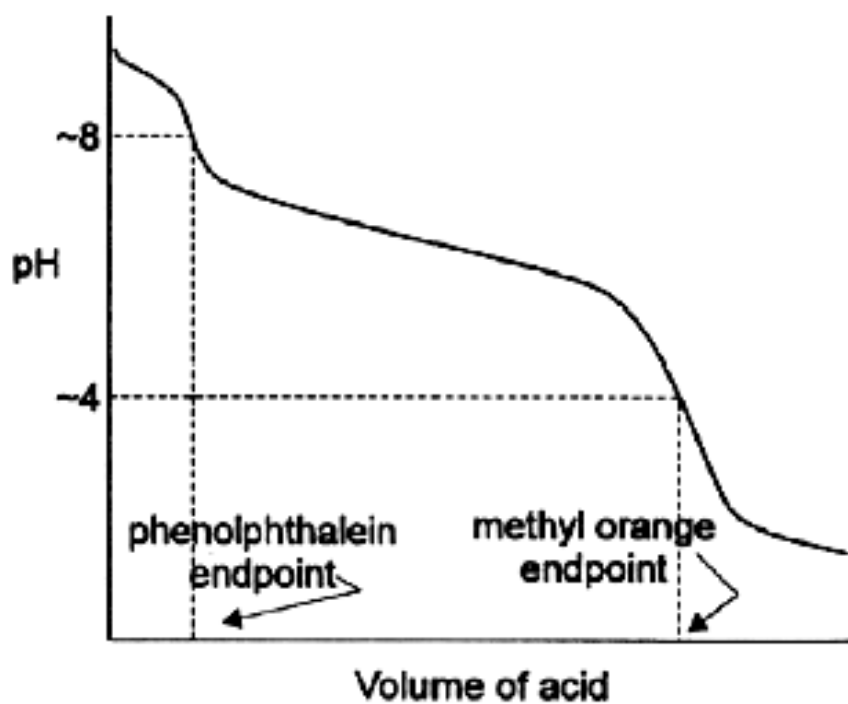
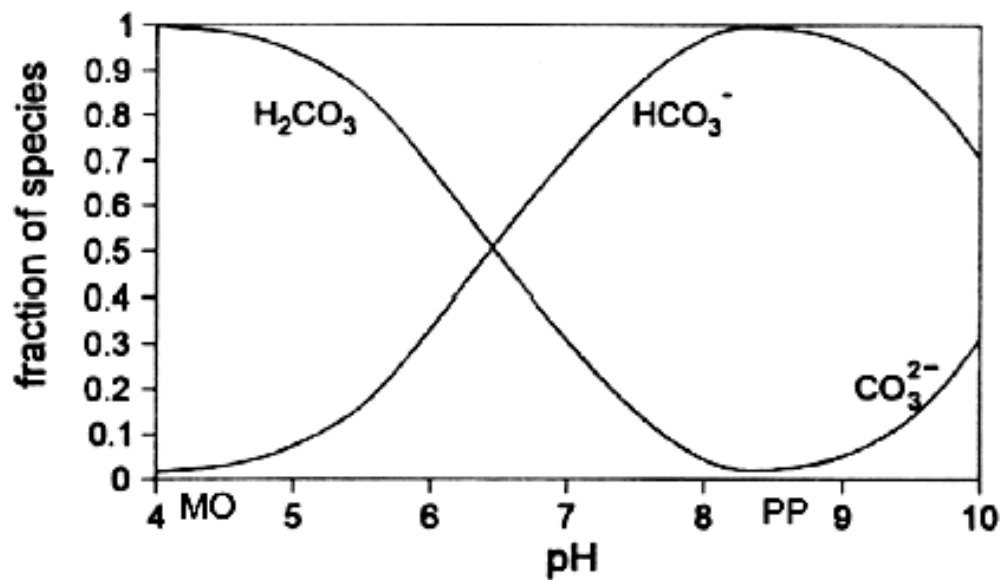
- More complex than O<sub>2</sub> because CO<sub>2</sub>(aq) ~ H<sub>2</sub>CO<sub>3</sub>(aq), which can dissociate through acid-base equilibria
- CO<sub>2</sub>(g) + H<sub>2</sub>O(l) ↔ H<sub>2</sub>CO<sub>3</sub>(aq)
  - KH = 3.4 x 10<sup>-2</sup> mol L<sup>-1</sup> atm<sup>-1</sup>
- H<sub>2</sub>CO<sub>3</sub>(aq) ↔ H<sup>+</sup>(aq) + HCO<sub>3</sub><sup>-</sup>(aq)
  - K<sub>a</sub> = 4.2 x 10<sup>-7</sup> mol L<sup>-1</sup>

Total dissolved carbonate increases as pH rises



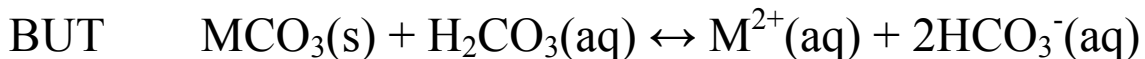
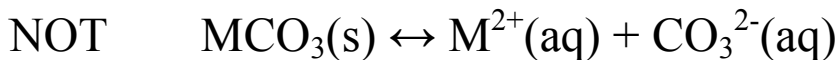
## *Alkalinity*

- Of water is a measure of the concentration of all bases in the water, not its pH
  - determined largely by the strongest base present
  - text pp. 140-142
- Alkalinity is measured by titrating the water against standard acid / moles / concentration of  $H^+$  needed to neutralize the bases
- Phenolphthalein alkalinity is the amount of acid needed to reach the phenolphthalein endpoint (pH 8.5) remembering that titration is from high to low pH
- Total alkalinity is the amount of acid needed to reach the methyl orange endpoint (pH 4)
- If there are no other bases present (as in e.g., industrial waste water), the phenolphthalein endpoint measures mostly  $CO_3^{2-}$  the methyl orange endpoint measures  $CO_3^{2-} + HCO_3^-$
- Two measurements to determine both  $CO_3^{2-} + HCO_3^-$ 
  - both total and phenolphthalein alkalinity or
  - one of the above plus pH  $\rightarrow$  ratio  $[CO_3^{2-}]/[HCO_3^-]$



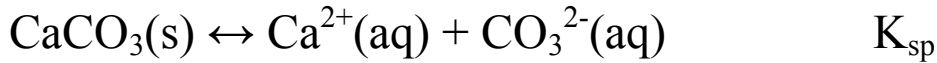
## ***Hardness***

- Is a measure of the concentration of “hardness ions” (mainly  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) that form insoluble salts, especially carbonates: text, pp. 142-146.
- Analysis of hardness ions:
  - titration against  $\text{EDTA}^{4-}$  using Eriochrome Black T indicator (Ca only)
  - atomic absorption spectroscopy
- Origin of hardness ions:
  - dissolution of gypsum
  - $\text{CaSO}_4(\text{s}) \leftrightarrow \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
  - dissolution of limestone rocks:  $\text{CaCO}_3$  (limestone);  $\text{CaCO}_3 \cdot \text{MgCO}_3$  (dolomite)



- Note  $p(\text{CO}_2)$  underground is often much greater than 370 ppmv
- In what follows, note the text, footnote 8, p. 143 about  $K_{\text{sp}}$  calculations
  - $\text{CaSO}_4$   $K_{\text{sp}} = 4 \times 10^{-5} (\text{mol/L})^2$
  - $\text{CaCO}_3$   $K_{\text{sp}} = 6 \times 10^{-9} (\text{mol/L})^2$
  - $\frac{1}{2}\text{CaCO}_3 \cdot \text{MgCO}_3$   $K_{\text{sp}} = 5 \times 10^{-7} (\text{mol/L})^2$

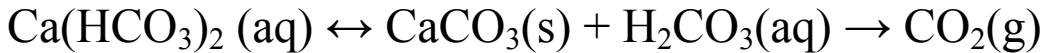
### ***Dissolution of CaCO<sub>3</sub>***



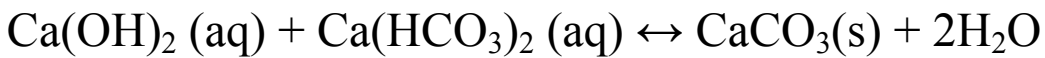
- Net:  $\text{CaCO}_3(\text{s}) + \text{H}_2\text{CO}_3(\text{aq}) \leftrightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{HCO}_3^-(\text{aq})$
- or,  $\text{CaCO}_3(\text{s}) + \text{H}_2\text{CO}_3(\text{aq}) \leftrightarrow \text{Ca}(\text{HCO}_3)_2(\text{aq})$
- K for net reaction =  $K_{\text{sp}} \times K_{\text{a1}}/K_{\text{a2}} = 5 \times 10^{-5} (\text{mol L}^{-1})^2$ 
  - when expressed as “ppm of CaCO<sub>3</sub>”, values up to 300 ppm are obtained in hard water areas
  - Hard water
    - contains hardness ions
    - usually limestone areas
      - Southern Ontario
  - Soft water
    - low concentrations of hardness ions
    - sandstone and granite areas
      - Northern and Eastern Ontario
- All water must have a balance of cations and anions; therefore, hard water is usually well buffered against acidification
  - Relatively high concentrations of weak bases
  - Alkalinity is a measure of buffering capacity
    - High alkalinity usually correlates with high hardness

## ***Water Softening***

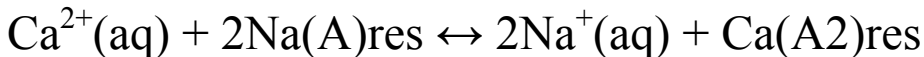
- Required for steam boilers due to deposition of salts
- When hard water is heated:



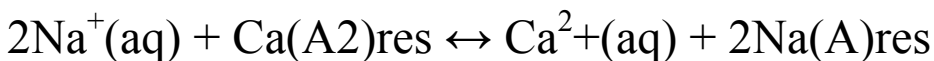
- Water softening is the process of removing hardness ions
- Lime Softening (industrial use only): neutralize  $\text{HCO}_3^-$  with  $\text{OH}^-$



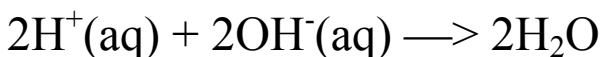
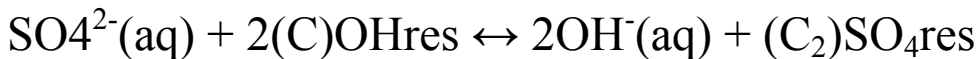
- Ion exchange resins:
  - Na(A), where (A) = polymeric anion
    - $\text{Ca}^{2+}$  removal through cation exchange



- Resin regeneration with concentrated brine:



- Deionized water: cation and anion exchangers in series, using  $\text{H}^+$  form of the cation exchanger and  $\text{OH}^-$  form of the anion exchanger – example of  $\text{CaSO}_4$



## *Seawater*

- A solution of high ionic strength
  - The main environment encountered where *activities* (*a*) must be used rather than concentration
- Ion (conc, mol/L)
  - $\text{Na}^+$  (0.46)
  - $\text{K}^+$  (0.010)
  - $\text{Mg}^{2+}$  (0.054)
  - $\text{Ca}^{2+}$  (0.010)
  - $\text{Cl}^-$  (0.55)
  - $\text{SO}_4^{2-}$  (0.028)
  - $\text{HCO}_3^-$  (0.0023)
  - $\text{CO}_3^{2-}$  (0.0003) included with  $\text{HCO}_3^-$
- Ocean water approximately in equilibrium with  $\text{CaCO}_3$ , but  $Q_{\text{sp}} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] \gg K_{\text{sp}}$ : text, p. 150
- First reason:  $a(\text{Ca}^{2+})$  and  $a(\text{CO}_3^{2-}) < [\text{Ca}^{2+}][\text{CO}_3^{2-}]$ 
  - i.e.,  $\gamma(\text{Ca}^{2+}) \sim 0.26$ ;  $\gamma(\text{CO}_3^{2-}) \sim 0.20$
- Second reason: complexation: formation of species such as:
  - $(\text{CaSO}_4)$ : 8% of total Ca;  $(\text{CaHCO}_3)^+$ : 1% of total Ca
  - $(\text{MgCO}_3)$ : 64% of total  $\text{CO}_3$ ;  $(\text{NaCO}_3)^-$ : 19% of total  $\text{CO}_3$ ;
  - $(\text{CaCO}_3)$ : 7% of total  $\text{CO}_3$

## ***Irrigation and water quality***

- Read text pp. 147-149
- Read article from The Economist, link to internet = [http://www.economist.com/displaystory.cfm?story\\_id=1906914](http://www.economist.com/displaystory.cfm?story_id=1906914)

## ***Properties of Water***

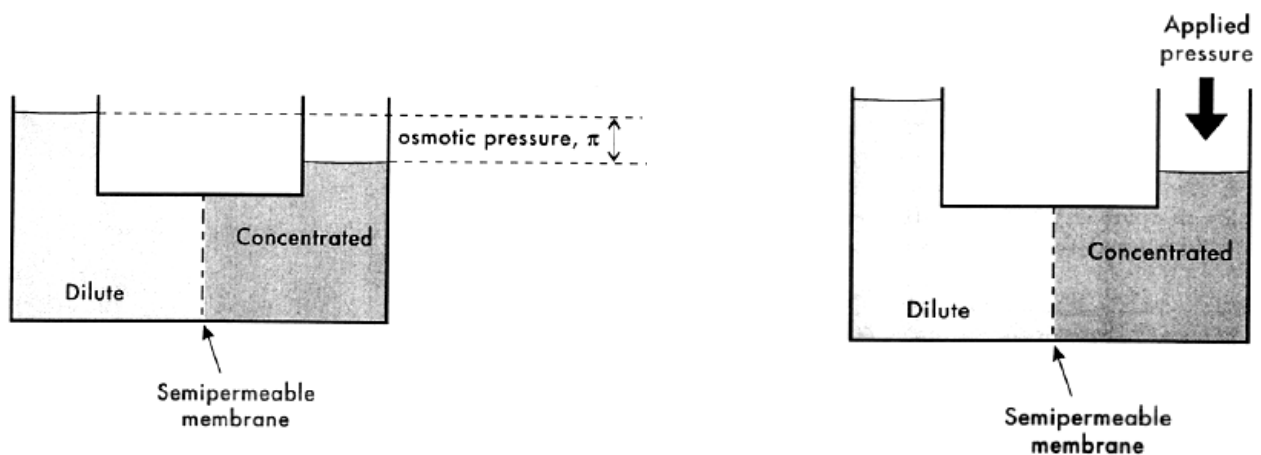
- Amounts on Earth:
- Oceans,  $\sim 10^{20}$  mol Rivers and lakes,  $\sim 10^{15}$  mol

## ***Freezing point depression***

- Solutes depress the freezing point of water
  - $\Delta T = K_f \times m$ 
    - $K_f$  = molal freezing point depression constant, units  $\text{K kg mol}^{-1}$
    - $m$  = molal concentration of solute,  $\text{mol kg}^{-1}$
- The freezing point depression is independent of the identity of the solute. For ionic solutes consider all the ions separately, e.g., for NaCl there are two solutes to consider,  $\text{Na}^+$  and  $\text{Cl}^-$
- Applications
  - road salt
  - trees in winter
  - fish in polar oceans
  - laboratory: determining molar mass

## *Osmosis and Reverse Osmosis*

- Osmosis
- osmotic pressure  $\pi = c \times RT$ 
  - $c$  in  $\text{mol L}^{-1}$
  - $R$  in  $\text{L atm mol}^{-1} \text{K}^{-1}$
  - $\pi$  in atm
- osmotic pressure independent of the solute identity
  - applications
    - water rise in trees
    - hypertonic and hypotonic solutions;
    - impact on cells
    - laboratory: measuring molar mass of polymers and biopolymers
- Reverse osmosis: a method of water purification



## Aqueous Atmospheric Chemistry

- Aqueous Atmospheric Chemistry: Acid Rain
- Review Henry's Law:
  - Scavenging of water-soluble gases / vapours into clouds, fogs, and rain
- Review normal pH of rainwater ~ 5.6 due to dissolved CO<sub>2</sub>
- Acid precipitation a result of industrial activities: emission of SO<sub>2</sub> and NO
- One major route to NO<sub>x</sub> deposition: gas phase oxidation
  - Recall formation of HNO<sub>3</sub> from NO<sub>2</sub>
- Several routes to SO<sub>2</sub> deposition
  - Gas or aqueous phase oxidation
- SO<sub>2</sub>(g) + H<sub>2</sub>O → H<sub>2</sub>SO<sub>3</sub>(aq) → deposition
- SO<sub>2</sub>(g) + OH• → SO<sub>3</sub>(g) (+H<sub>2</sub>O) → H<sub>2</sub>SO<sub>4</sub>(aq) → deposition
- SO<sub>2</sub>(g) + H<sub>2</sub>O → H<sub>2</sub>SO<sub>3</sub>(aq) (+O) → H<sub>2</sub>SO<sub>4</sub>(aq) → deposition
- Acid rain long recognized as a problem; “the” air pollution problem of the ‘80s, but it is still with us



- “The Inco Superstack ( $46^{\circ}28'48.23''\text{N}$ ,  $81^{\circ}3'23.43''\text{W}$ ) is the tallest freestanding chimney in the Western hemisphere, with a height of 381 m (1,257 ft). (The chimney of the GRES-2 Power Station is the world's tallest). It was constructed by Inco Limited in 1972 at an estimated cost of 25 million dollars. The Superstack sits atop the largest nickel smelting operation in the world at Inco's Copper Cliff processing facility in the city of Greater Sudbury.”
- “The structure was built to disperse sulphur gases and other byproducts of the smelting process away from the city itself. As a result, these gases can be detected in the atmosphere around Greater Sudbury in a 150 mile radius of the Inco plant.”
- “Prior to the construction of the Superstack, the waste gases caused the landscape around Sudbury to be devoid

of any trees. The Superstack allowed the city, which for many years had a reputation as a barren, rocky wasteland, to launch an environmental reclamation plan which has included rehabilitation of water bodies such as Lake Ramsey, and an ambitious greening plan which has seen over three million new trees planted in the city. In 1992, the city was given an award by the United Nations in honour of its environmental rehabilitation programs.”

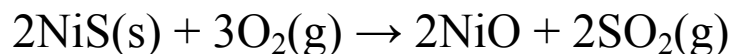
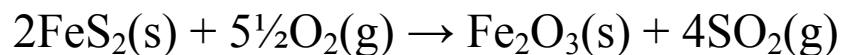
- “The GRES-2 Power Station is a Power Station in Ekibastuz, Kazakhstan. It has the world's tallest chimney at 419.7 meters high and was built in 1987. The chimney beats the Inco Superstack by about 38 meters.”

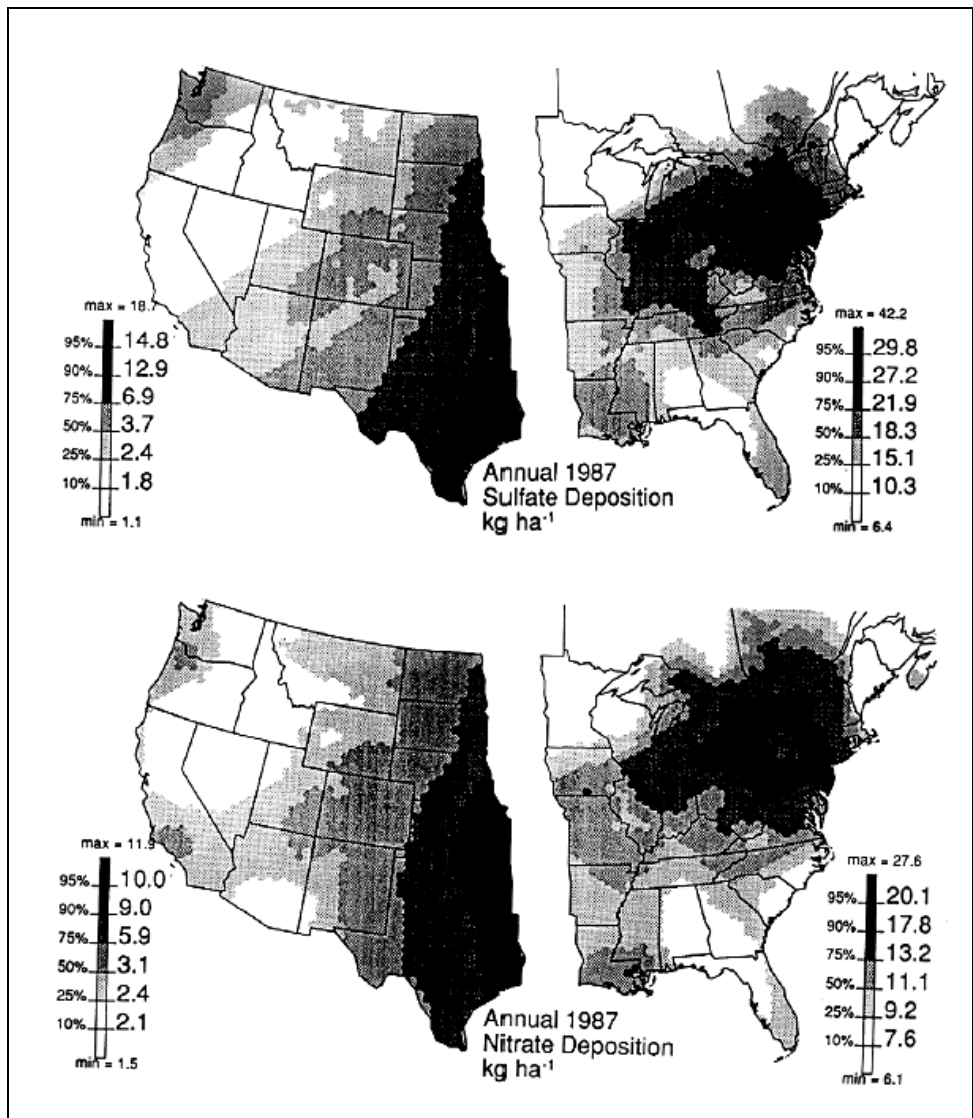
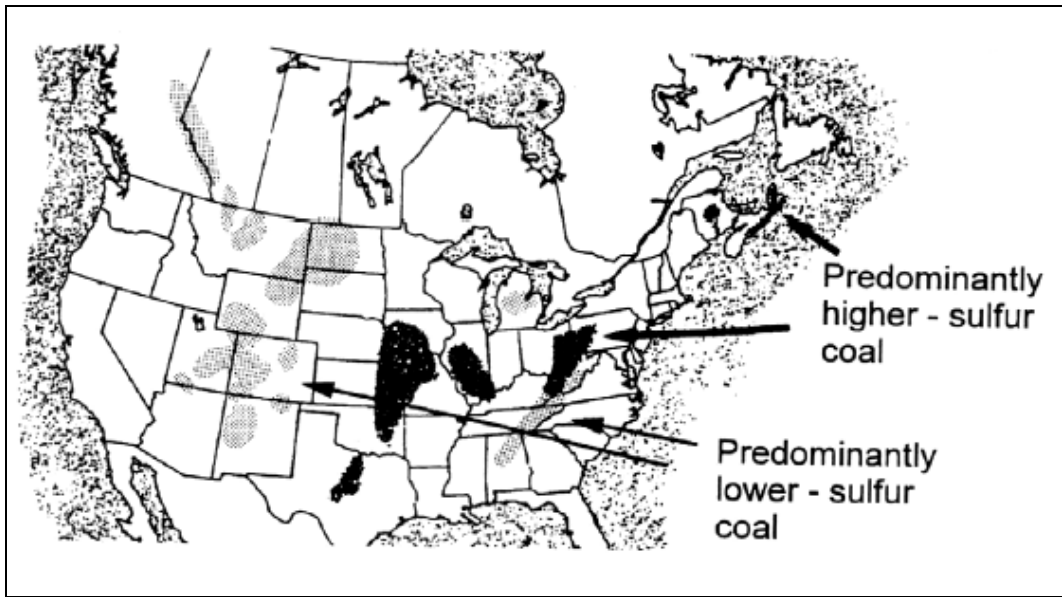
### *Sources of “acidic gas” emissions*

- NO<sub>x</sub>
  - All combustion processes, but especially: transportation, power generation, metal smelting



- SO<sub>2</sub>
  - coal as a fuel (typically 2-3% sulfur by mass)
  - smelting sulfidic metal ores: many commercially important metals occur as sulfides: Cu, Ni, Pb, Zn





### ***Importance of aqueous atmospheric chemistry***

- High surface to volume ratio of small droplets assures rapid approach to equilibrium:  $S/V = 3/r$
- Removal of soluble species from the gas / vapour phase reduces their gas phase concentrations, slowing reaction rates
  - scavenging of  $\text{HO}_2$  slows the rate of gas phase oxidation of NO
  - lower concentration of PAN in foggy air because  $\text{CH}_3\text{CO.OO}$  is scavenged into the aqueous phase
- Permanent removal if the droplet falls as rain (e.g.,  $\text{HNO}_3$ )
- Possibility of ionic reaction mechanisms in solution (e.g., hydrolysis of  $\text{N}_2\text{O}_5$ ; oxidation of  $\text{SO}_2$  by  $\text{H}_2\text{O}_2$ )
- Scattering light by droplets reduces light intensity, especially deep in a cloud, lowers  $J(\text{O}_3)$  and  $J(\text{NO}_2)$

## *Chemistry of Acid Rain*

For  $\text{CO}_2$

- $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_2\text{CO}_3(\text{aq})$ 
    - $K_{\text{H}} = 3.4 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$
  - $\text{H}_2\text{CO}_3(\text{aq}) \leftrightarrow \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$ 
    - $K_{\text{a}} = 4.2 \times 10^{-7} \text{ mol L}^{-1}$
- 
- $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$ 
    - $K_{\text{c}} = 1.4 \times 10^{-8} \text{ mol}^2 \text{ L}^{-2} \text{ atm}^{-1}$

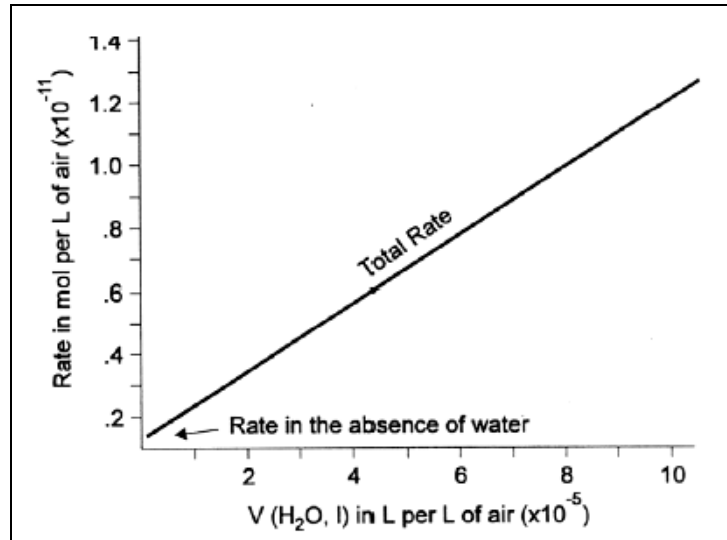
For  $\text{SO}_2$

- $\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_2\text{SO}_3(\text{aq})$ 
    - $K_{\text{H}} = 1.2 \text{ mol L}^{-1} \text{ atm}^{-1}$
  - $\text{H}_2\text{SO}_3(\text{aq}) \leftrightarrow \text{H}^+(\text{aq}) + \text{HSO}_3^-(\text{aq})$ 
    - $K_{\text{a}} = 1.7 \times 10^{-2} \text{ mol L}^{-1}$
- 
- $\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}^+(\text{aq}) + \text{HSO}_3^-(\text{aq})$ 
    - $K_{\text{c}} = 2.1 \times 10^{-2} \text{ mol}^2 \text{ L}^{-2} \text{ atm}^{-1}$
- 
- In summary, low (ppbv) concentrations of  $\text{SO}_2(\text{g})$  change the pH of rainwater more than 375 ppmv of  $\text{CO}_2$  because:
    - $\text{SO}_2$  more soluble in water than  $\text{CO}_2$  ( $K_{\text{H}}$ )
    - $\text{H}_2\text{SO}_3$  stronger acid than  $\text{H}_2\text{CO}_3$  ( $K_{\text{a}}$ )

## ***Oxidation of SO<sub>2</sub>***

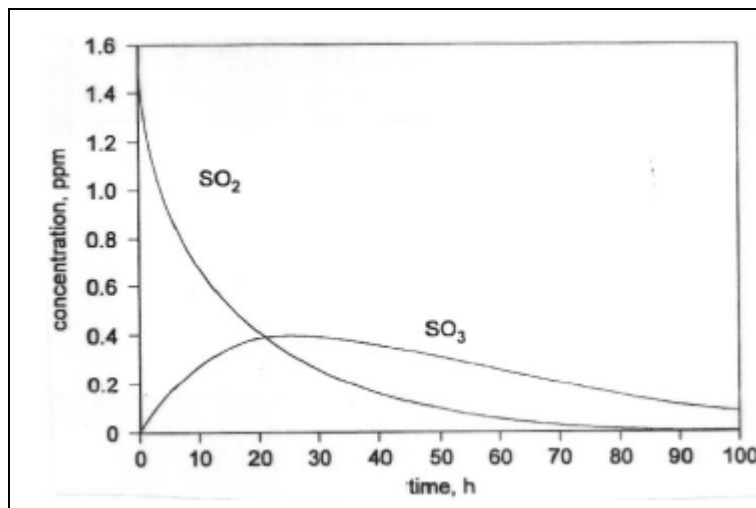
- Major oxidation route for SO<sub>2</sub> in ***dry air***:
- SO<sub>2</sub>(g) + OH → SO<sub>3</sub>(g) + (H<sub>2</sub>O) → H<sub>2</sub>SO<sub>4</sub>(aq) → deposition
- Details:
- SO<sub>2</sub>(g) + OH<sup>•</sup> (g) → HSO<sub>3</sub>(g)
  - $k = 9 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$
- HSO<sub>3</sub>(g) + O<sub>2</sub>(g) → SO<sub>3</sub>(g) + HO<sub>2</sub>(g)
  - Oxidation rate:  $k' \sim 10^{-6} \text{ s}^{-1} \rightarrow t_{1/2} \sim 7 \times 10^5 \text{ s}$  (8 days)
- Major oxidation route for SO<sub>2</sub> in ***wet (humid) air***:
- SO<sub>2</sub>(g) + H<sub>2</sub>O → H<sub>2</sub>SO<sub>3</sub>(aq) + (O) → H<sub>2</sub>SO<sub>4</sub>(aq) → deposition
- Details:
  - SO<sub>2</sub>(g) → H<sub>2</sub>SO<sub>3</sub>(aq)
  - 2HO<sub>2</sub> → H<sub>2</sub>O<sub>2</sub> + O<sub>2</sub> [in gas or aqueous phase]
  - H<sub>2</sub>SO<sub>3</sub>(aq) + H<sub>2</sub>O<sub>2</sub> → H<sub>2</sub>SO<sub>4</sub>(aq) + H<sub>2</sub>O
    - [strongly pH dependent; faster at higher pH]
  - Aqueous phase oxidation by O<sub>3</sub> is slower
- Oxidation rate: up to 10-30% per hour ( $t_{1/2} \sim 2-7 \text{ h}$ ); typical oxidation rates 0.01-0.1 h<sup>-1</sup> ( $t_{1/2} \sim 2-20 \text{ h}$ ).
- Summary: acid precipitation is a regional problem.

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



***$SO_2$  pollution: a regional problem***

- if  $t_{1/2} \sim 2-20$  h, and wind speed  $\sim 20$  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  $\sim 2000$  km

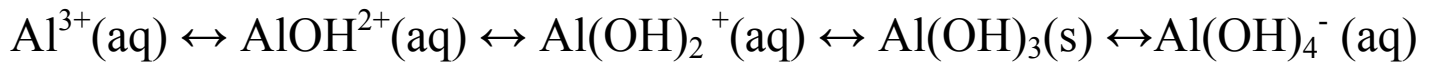
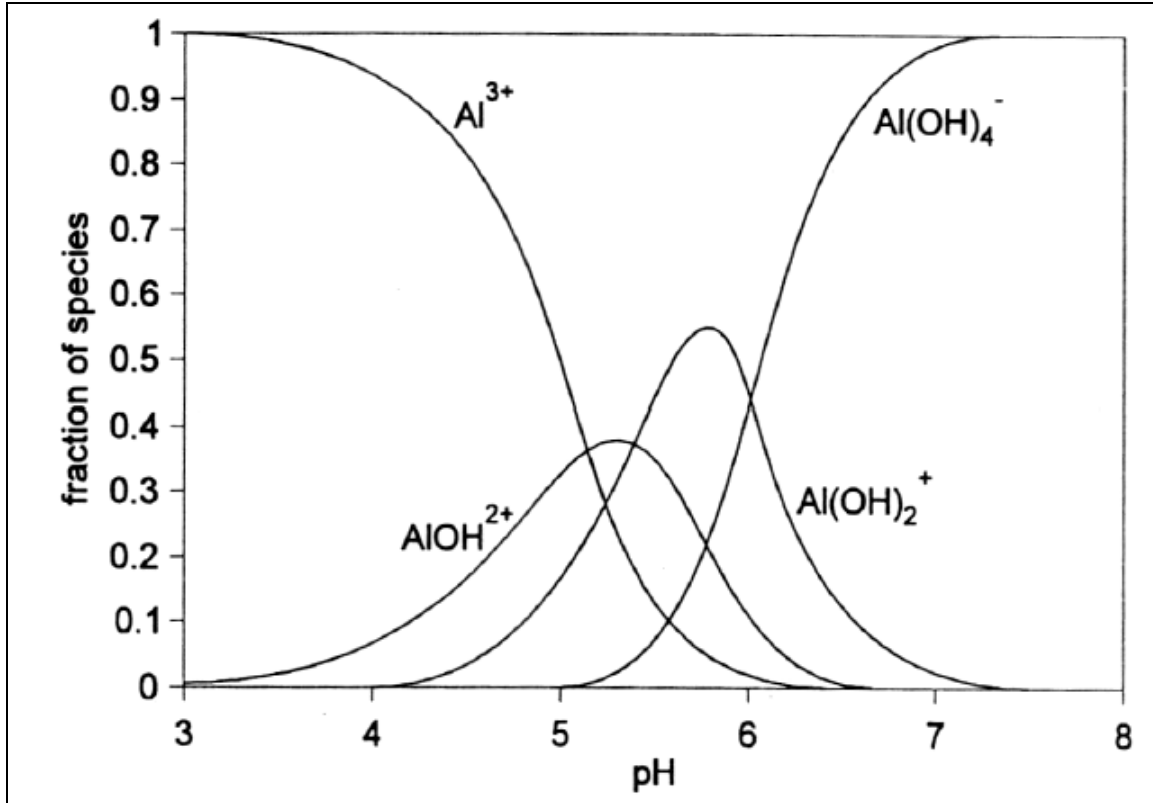


## *Effects of acidic emissions*

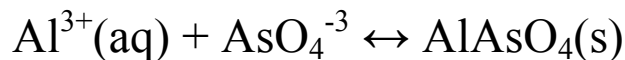
- effects on plants, on aquatic life, through lowering pH
- susceptible and non-susceptible lakes:  $\text{CaCO}_3$  as a buffer
  - natural erosion of caves and gorges
- $\text{CaCO}_3(\text{s}) + \text{H}_2\text{CO}_3(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{HCO}_3^-(\text{aq})$ 
  - $K = 5.3 \times 10^{-5} (\text{mol L}^{-1})^2$  at  $25^\circ\text{C}$
- lakes and streams underlain by  $\text{CaCO}_3(\text{s})$  have high natural alkalinity
  - When acidification occurs:
    - $\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{CO}_3(\text{aq}) \rightarrow \text{CO}_2(\text{g})$
    - the  $\text{HCO}_3^-(\text{aq})$  that is consumed is replaced by dissolution of more  $\text{CaCO}_3$
- effects on structures, especially limestone and steel
- Net reaction for limestone can be written as:
  - $\text{CaCO}_3(\text{s}) + \text{H}^+(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{HCO}_3^-$ 
    - $K = 1.3 \times 10^2 \text{ mol L}^{-1}$  at  $25^\circ\text{C}$
- in the case of sulfur oxide emissions, “sulfation” leads to flaking off from the surface
- $\text{CaCO}_3(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) + \text{SO}_2(\text{g}) \rightarrow \text{CaSO}_4(\text{s})$
- Please review text pp. 176-182: natural waters and aluminum solubility

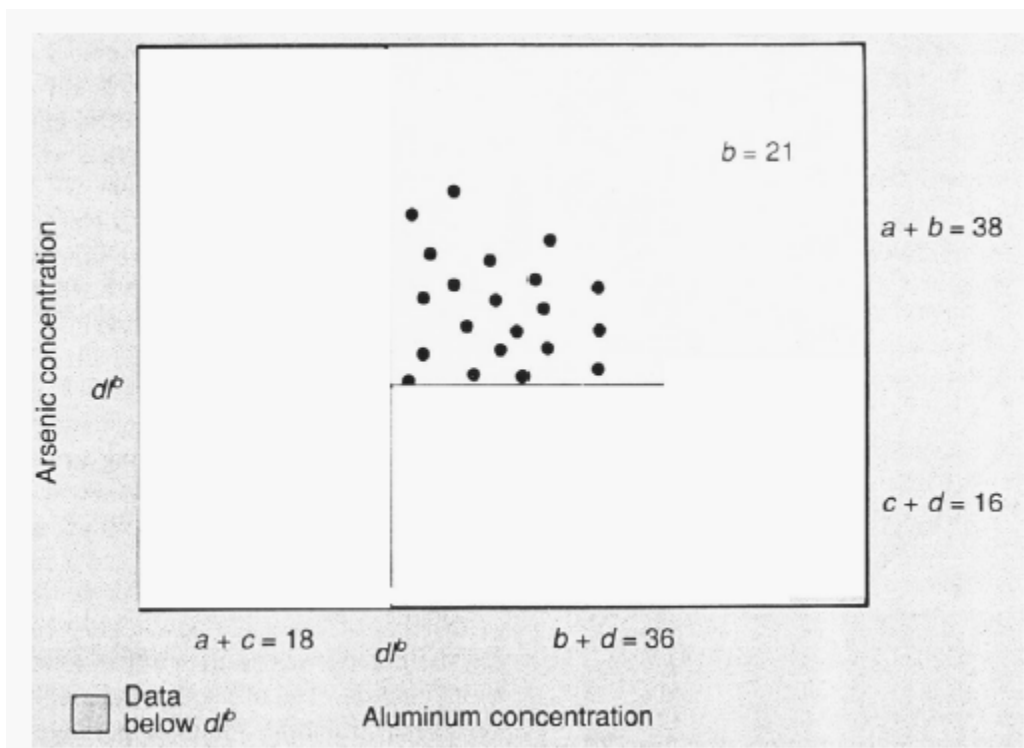
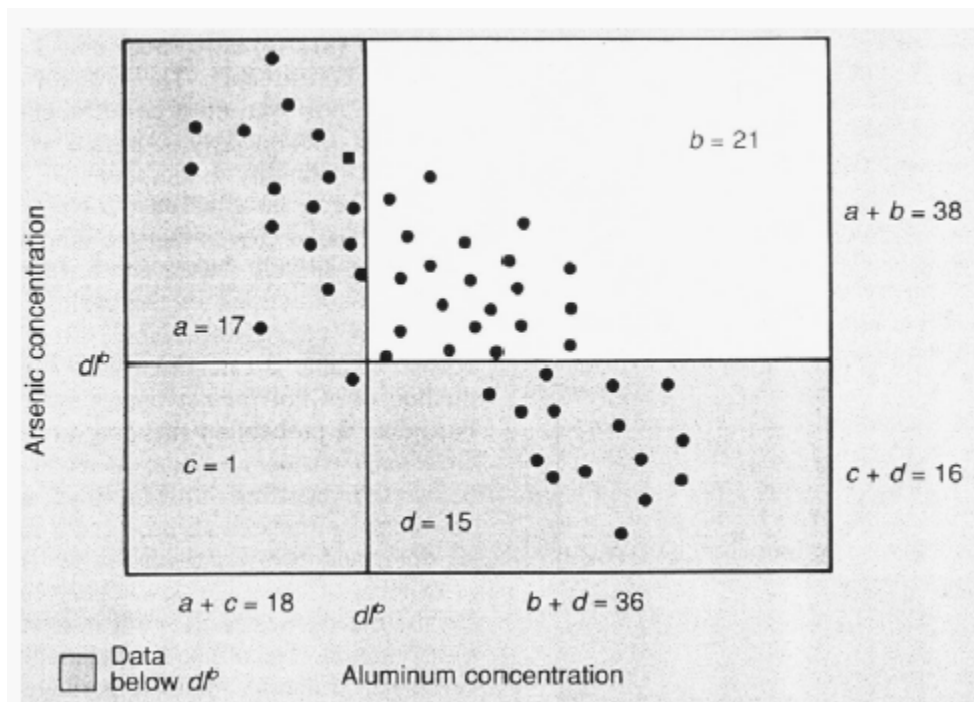
## Aluminum solubility

- Aluminum speciation: solubility minimum near pH 6.5



- Fluoride raises the overall solubility of aluminum:
  - aluminum smelters which can release HF
- Arsenic lowers the concentration of dissolved aluminum:
  - Environ. Sci. Technol. 1990, p. 1774
  - simplified expression...





## *Abatement of acidic emissions*

- NO<sub>x</sub>
  - New technology involving ammonia injection into the exhaust gas stream:
$$\text{NO}_x + \text{NH}_3 \rightarrow \text{N}_2 + \text{H}_2\text{O} \text{ (unbalanced)}$$
    - Proposed use at Southdown gas-fired generating station in Mississauga; issues with highly polluting Lakeview and Nanticoke stations
- Particularly useful for gas-fired plants where there is no SO<sub>2</sub> in the flue gases

## **SO<sub>2</sub> from coal as a fuel**

- Combustion of 1 tonne of coal that is 2% sulfur by mass
- 80,000 mol CO<sub>2</sub>
- 320,000 mol N<sub>2</sub>
- 600 mol of SO<sub>2</sub> (~0.15% of the total: uneconomic to recover)
- **Flue Gas Desulfurization (FGD)**
  - technology to remove SO<sub>2</sub>
  - pass a slurry of ground lime or limestone down the stack as the hot flue gases pass upwards
    - $\text{SO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSO}_3 + \text{H}_2\text{O}$
    - Also,  $\text{SO}_2 + \text{Ca}(\text{OH})_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O}$
    - $\text{SO}_2 + \text{CaCO}_3 \rightarrow \text{CaSO}_3 + \text{CO}_2$

## ***Improved combustion methods***

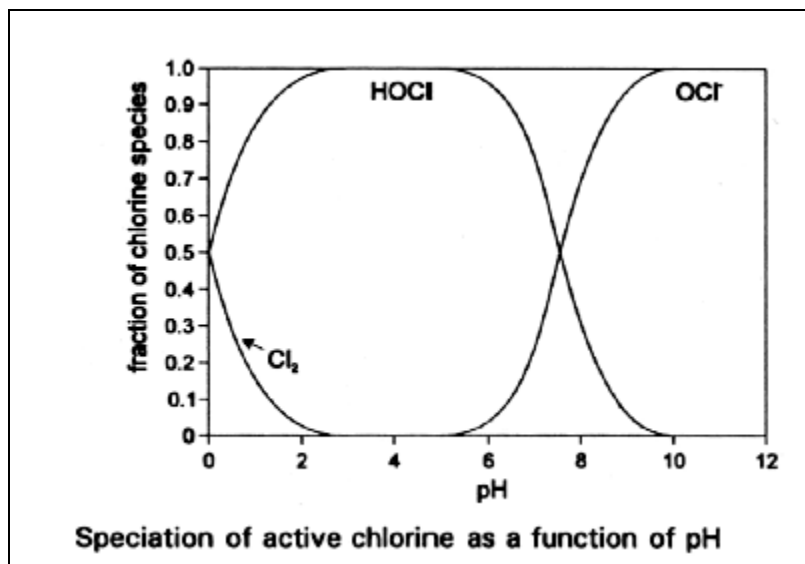
- coal cleaning:
  - separate finely divided coal particles by froth flotation, since coal has  $d = 2.3 \text{ g cm}^{-3}$  while pyrite  $\text{FeS}_2$ , the main sulfur species has  $d = 4.5 \text{ g cm}^{-3}$
- fluidized bed combustion:
  - mix finely ground coal with limestone and burn the fine particles on a screen so that the particles are supported by the combustion air train. Sulfur in the coal  $\rightarrow \text{CaSO}_3 / \text{CaSO}_4$
- **$\text{SO}_2$  from metal refining**
  - Problem is sulfide ores
- e.g.  $2\text{FeS}_2(\text{s}) + 5\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{Fe}_2\text{O}_3(\text{s}) + 4\text{SO}_2(\text{g})$
- $2\text{NiS}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{NiO} + 2\text{SO}_2(\text{g})$
- Unlike coal combustion, there is enough  $\text{SO}_2$  to collect as  $\text{SO}_2(\text{l})$  or to convert into  $\text{H}_2\text{SO}_4$ . Both of these are very cheap commodity chemicals;  $\text{H}_2\text{SO}_4$  by this route must compete with purer material from virgin sulfur or natural gas sweetening.
- $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \leftrightarrow \text{SO}_3(\text{g})$  [ $\text{V}_2\text{O}_5$  catalyst,  $450^\circ\text{C}$ ]
- $\text{SO}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{H}_2\text{SO}_4 \cdot \text{SO}_3(\text{l}) + (\text{H}_2\text{O}) \rightarrow \text{H}_2\text{SO}_4$

## Drinking Water

- Water types
  - surface water (rivers and lakes)
  - ground water (wells)
- Making water fit for consumption
  - clarification
  - microorganisms: sewage, animal waste
  - natural contaminants
    - arsenic
  - industrial and agricultural pollutants
- Municipal water treatment
  - primary and settling tanks
  - aeration
  - coagulation (secondary settling)
  - disinfection
- Aeration
  - removes easily oxidizable substances, which would otherwise be a problem for disinfection procedures
    - iron a problem
      - $\text{FeS}_2$  or  $\text{FeCO}_3$ : iron(II)
    - iron is the source of staining and “metallic taste” for people who have domestic wells: use filters
    - iron(II) oxidation a function of pH:

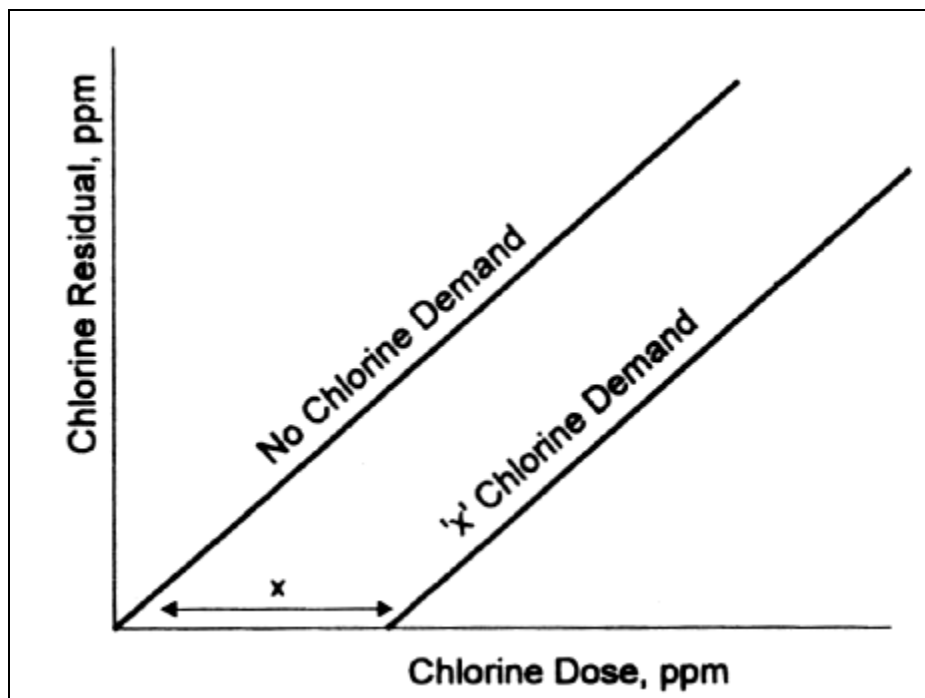
- Coagulation
  - removal of pollen, bacteria, spores, many viruses, colloidal minerals
  - gives water a sparkling appearance
  - use of filter alum:
    - $\text{Al}_2(\text{SO}_4)_3$  or less commonly ferric salts, e.g.,  $\text{Fe}_2(\text{SO}_4)_3$ 
      - recall minimum solubility of  $\text{Al}(\text{OH})_3$  at pH 6-7
  - $\text{Al}^{3+}(\text{aq}) + 3\text{HCO}_3^-(\text{aq}) \rightarrow \text{Al}(\text{OH})_3(\text{s}) + 3\text{CO}_2(\text{g})$
  - $\text{Al}(\text{OH})_3(\text{s})$  is a gelatinous precipitate that entraps small particles as it settles
  - $\text{Fe}(\text{OH})_3(\text{s})$  is similar
    - insoluble at pH > 3, except in very acidic media
      - $K_{\text{sp}} \sim 10^{-38} (\text{mol L}^{-1})^4$
- Disinfection
  - kills residual bacteria and viruses
  - maintains the water clean in the distribution system (up to 1 week in a large system: “chlorine residual”)
  - dirty water is the cause of millions of deaths every year, especially among children
  - clean water the greatest public health achievement ever: cholera observed in Canada even in 1900.
  - Walkerton (>10 deaths)

- Disinfection with chlorine
  - probably the cheapest and one of the most effective; maintains a chlorine residual



- $\text{Cl}_2(\text{aq}) \rightarrow \text{HOCl}(\text{aq}) \rightarrow \text{ClO}^-(\text{aq})$
- $\text{HOCl}(\text{aq})$  about  $10\times$  more effective than  $\text{ClO}^-(\text{aq})$ 
  - Due to the fact that  $\text{HOCl}$  can cross bacterial membranes more easily because it is more lipophilic than  $\text{Cl}_2$
- water with  $\text{pH} > 7.5$  requires more chlorine – or longer disinfection times than does water with  $\text{pH} < 7.5$
- Terms:
  - chlorine dose = concentration originally used
  - chlorine residual = concentration in the finished water
  - chlorine demand = concentration consumed by
  - oxidizable substances present in the water

- free available chlorine is the sum of concentrations of HOCl(aq) and ClO<sup>-</sup>(aq)



### Chlorine Dose, Chlorine Demand, Residual Chlorine

- The typical residence time of chlorine at the chlorination plant < 1 h
- The typical concentration of chlorine in the finished water < 1 ppm
- Disadvantages of using chlorine
  - Taste and odour problems, mostly from chlorinated phenols
- Significant products of chlorination
  - trihalomethanes
    - chloroform CHCl<sub>3</sub>

- present at 10 ppb or more.
  - Source is natural substances (humic acids)
    - Chloroform is a hepatocarcinogen
- $>C(=O)CH_3 + 3HOCl \rightarrow CO_2^- + CHCl_3 + 2H_2O$
- US DHHS Report, 1995:
- Alternatives to chlorination
  - Ozone
  - Chlorine dioxide
  - UV irradiation
  - Chloramines
- Chlorine dioxide
  - Unstable, must be made in situ

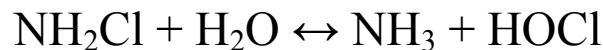


- an oxidizing agent, not a chlorinating agent
  - no taste
    - $ClO_2 + \text{substrate} \rightarrow ClO_2^- + \text{substrate}^+$
- can be used as a temporary expedient when taste and odour problems occur
  - purchase sodium chlorite
    - storage issues
  - some question about its effectiveness vs Giardia and Cryptosporidium
- issues concerning toxicity (text, p. 209)

- Ozonation (Ozone)
  - Unstable, must be made in situ
    - Electric discharge on dry O<sub>2</sub> (air)
 
$$3\text{O}_2 \rightarrow 2\text{O}_3$$
      - Formed as a dilute mixture in air
  - Ozonation equipment is expensive, only economic on a large scale
  - Ozone is an oxidizing agent, not a chlorinating agent
    - No taste and odour problems, but cannot be used like ClO<sub>2</sub> as a temporary replacement for chlorine
  - No residual levels detected in the water
    - Decomposition is pH dependent
  - Also faster at higher water temperature
  - Concerns over formation of aldehydes following disinfection

### Chloramine: NH<sub>2</sub>Cl

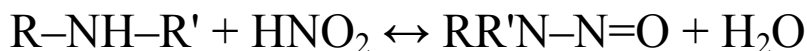
- Used in domestic applications ... cottages, as a source of “available chlorine”



- UV radiation
  - uses UV-C at 254 nm
    - mercury discharge lamp (germicidal lamps)
  - kills microorganisms by photochemical cross-linking of DNA, which absorbs strongly at this wavelength
  - unlike preceding methods, uses a simple flow-through system (no holding tank) because contact time is short (seconds)
  - not influenced by pH or temperature
  - applicable to large and small scale installations, even domestic use
  - water must be clear and free of absorbing solutes
- Analysis of  $\text{Cl}_2$ ,  $\text{ClO}_2$ ,  $\text{NH}_2\text{Cl}$  and  $\text{O}_3$ 
  - iodometric titration
- Drinking Water Quality
  - Standards (US) vs Guidelines (Canada)
- Metals in drinking water
- solubilization in acidic waters
  - most are cumulative poisons (rate of excretion is slow):
    - Hg, Pb, Cd, Cu, As
  - lead a problem in older homes (“plumbing”/solder)
  - lead and mental retardation (also lead-based paints)

- Soft water more of a problem: Pb slightly more electropositive than hydrogen
- First draw water – water in contact with lead solder, dissolves lead with increasing contact time – first plugs of water are rich in lead
- MAC in drinking water is 5 ppb
- Lead in Maple Syrup detected from older syrup concentrators
- Cadmium a relatively recent problem, with the use of Cd in electroplating and Ni-Cd rechargeable batteries
- Mercury as a problem more often associated with food intake than water
  - Particularly in fish
- Arsenic a serious problem, especially in parts of Asia: Bangladesh, Taiwan, Vietnam
  - Levels in Bangladesh recorded 1-5 ppm in some places
  - Problem associated with wells drilled to avoid drinking microbially-contaminated surface water skin eruptions, skin cancer, internal cancers,
  - “Blackfoot disease”, neurotoxicity: hundreds of thousands affected
  - Testing of wells for those safe to drink
  - WHO limit for arsenic: previously 50 ppb, lowered to 10 ppb. US controversy over reduction of limit to WHO. New standard effective February 2006.
    - Problem for certain municipalities

- Nitrate / Nitrite
  - A problem in rural areas or where extensive fertilization runoff is possible
    - Contamination of wells from fertilizer
    - 45 ppm (10 ppm of nitrate nitrogen)
  - Methemoglobinemia in infants can result in mental retardation
  - Active agent is actually nitrite formed by reduction of nitrate by intestinal bacteria
  - Nitrite ion can nitrosate amines and amides to carcinogenic nitrosamines



- Fluoride
  - Medication?
  - $F^- + Ca_5(PO_4)_3OH \rightarrow OH^- + Ca_5(PO_4)_3F$ 

hydroxylapatite

fluorapatite
  - Small “safety factor” between benefit and dental fluorosis
  - Dental health is improving in North America
    - Due to fluoridation?
      - Better promotion and sales of toothbrushes?