Acid Rain

Outline:

1. Constituents of rainwater
2. pH and pKa
3. Sources of acid rain
4. Adverse effects of acid rain
5. Controls

1: Constituents of rainwater

- Gases are soluble in water: Henry's law

$$X\,(g) \;+\; H_2O\,(l) \overset{K_H}{\rightleftharpoons} H_2XO\,(aq)$$
$$K_H = \frac{[H_2XO]}{P_X}$$

  - Examples

$$CO_2\,(g) \;+\; H_2O\,(l) \overset{K_H}{\rightleftharpoons} H_2CO_3\,(aq) \qquad K_H(CO_2) = 3.4 \cdot 10^{-2} \text{ mol/l-atm}$$
$$SO_2\,(g) \;+\; H_2O\,(l) \overset{K_H}{\rightleftharpoons} H_2SO_3\,(aq) \qquad K_H(SO_2) = 1.2 \text{ mol/l-atm}$$

- Important soluble gases: CO_2, SO_2 and NO_2 ($K_H(NO_2) = 6.4 \cdot 10^{-3}$ mol/l-atm)
  - Direct absorption of $NO_2\,(g)$ neglible: HNO_3 produced by action of hydroxy radical
- Major sources of soluble gases (reminder)
  - SO_2
    1. Coal burning

$$\text{coal} \;+\; O_2\,(g) \xrightarrow{\Delta} SO_2\,(g) \;+\; \text{electricty}$$

    2. Volcanos
  - NO_2
    1. Natural: microbial decomposition in soil, lightning
    2. Anthropogenic: transportation industry

pH and pKa

- $pH = -\log a_{H_3O^+} = -\log[H_3O^+]$.
- Hydrogen bonding in water leads to important physical properties:
    1. Density of ice lower than liquid water in range $T = 0-4$ C. Important in evolution of life
    2. Pressure dependence: applying pressure melts ice
    3. Hydrophobic and hydrophilic interactions: protein structure, membranes, micelles, ...
- H_3O^+ represents an excess proton in water.
    - Proton "solvated" by surrounding water molecules in cage-like structure
    - Rapid and complicated dynamics of proton motion in water
- $pKa = -\log K_a$, where K_a is the dissociative equilibrium constant for the reaction

$$HA\ (aq) + H_2O_l \overset{K_a}{\rightleftharpoons} H_3O^+\ (aq)\ +\ A^-\ (aq)$$

$$K_a = \frac{a_{H_3O^+}a_{A^-}}{a_{HA}a_{a_{H_2O}}} = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

    - Large $K_a \Longrightarrow$ lots of dissociation $\Longrightarrow$ strong acid.
- Key Point: solubility and strength of acid important for pH
    - Small amounts of SO_2 greatly affect pH since
        1. Very soluble in H_2O: large K_H
        2. Strong acids formed upon dissolving: H_2SO_4 and H_2SO_3.

Chemistry of Acid Rain

- NO_2 chemistry
  1. $NO_2 + OH \longrightarrow HNO_3$ (major route)
  2. $$\begin{aligned} NO_2 + O_3 &\longrightarrow NO_3 + O_2 \\ NO_3 + CH_4 &\longrightarrow HNO_3 + CH_3 \quad \text{(at night)} \end{aligned}$$
  3. $$\begin{aligned} NO_3 + NO_2 &\rightleftharpoons N_2O_5 \\ N_2O_5 + H_2O &\longrightarrow 2HNO_3 \end{aligned}$$

- SO_2 chemistry
  1. $SO_2\,(g) \ + \ H_2O\,(l) \overset{K_H}{\rightleftharpoons} H_2SO_3\,(aq)$
  2. $$\begin{aligned} SO_2 + OH &\xrightarrow{M} HSO_3 \quad \text{(addition reaction)} \\ HSO_3 + O_2 &\longrightarrow SO_3 + OOH \quad \text{(H abstraction)} \\ SO_3 + H_2O &\longrightarrow H_2SO_4 \end{aligned}$$
  3. $SO_2\,(aq) \ + \ H_2O_2\,(aq) \longrightarrow H_2SO_4\,(aq)$ in cloud (or fog)
  4. $SO_2 + \frac{1}{2}O_2 \xrightarrow{\text{surface}} SO_3$

- HCl: $HCl\,(g) \ + \ H_2O \longrightarrow HCl\,(aq)$

Primary cause of acid rain: SO_2 processes

- Occasionally HNO_3 more important when very high levels of NO_x-Southern California