

Materials To Remedy Environmental Pollutions

Graduate Course (445.686)

Seoul National University, 2008/1

Part 0. Environmental Pollutions

Chapter 1. Environmental Chemistry: a global perspectives

Chapter 1. Environmental Chemistry

1.1 Environmental composition: Aqueous solutions

- **Complications** in the use of **units** for the concentration of the composition
- **ppm** (parts per million)(cf. ppt, ppb): g of solutes per million milliliters of solution
 $= \mu\text{g mL}^{-1}$ or mgL^{-1}

E.g. 10 ppm aq. NH_4OH

$$= 10 \text{ mgNH}_4^+\text{L}^{-1} = 10 \times 10^{-3} \text{ gNH}_4^+\text{L}^{-1}$$

$$= 10 \times 10^{-3} / 18.0 \text{ molNH}_4^+\text{L}^{-1}$$

$$= 5.56 \times 10^{-4} \text{ mol NH}_4^+\text{L}^{-1}$$

Chapter 1. Environmental Chemistry

1.1 Environmental composition: Aqueous solutions

E.g. 10 ppm aq. NH_4OH

$$= 5.56 \times 10^{-4} \text{ mol } \text{NH}_4^+ \text{L}^{-1}$$

$$= 5.56 \times 10^{-4} \text{ mol } \text{NO}_3^- \text{L}^{-1} \text{ (1:1 conversion)}$$

$$= 5.56 \times 10^{-4} \times 62 \times 10^3 \text{ mg } \text{NO}_3^- \text{L}^{-1}$$

$$= 34 \text{ ppm } \text{NO}_3^-$$

(Δ is due to molar mass difference between NH_4^+ and NO_3^-)

$$= 34 \text{ mgNO}_3^- \text{L}^{-1} = 34 \times 14/62 \text{ mgNL}^{-1}$$

$$= 7.7 \text{ mgNL}^{-1} = 7.7 \text{ ppm}$$

(this is one way of avoiding complication abovementioned)

Chapter 1. Environmental Chemistry

1.1 Environmental composition: Aqueous solutions

- If molar concentration units are used, there will never be any confusion.

- Another limitation of 'parts per...':

they give no indication of the concentration of the reactive groups

E.g. Assumption : TOC in a forest stream = 9.0 mgCL^{-1}

COOH/g of humic material in water = 4 mmolg^{-1}

Carbon contents in humic material = 50 %

Then,

$$\text{TOC} = 9 \times 10^{-3} \times 100/50 \text{ g humic material/ L water}$$

$$= 9 \times 10^{-6} \times 100/50 \text{ g humic material/L}$$

$$\times 4 \times 10^{-3} \text{ mol COOH/g humic material}$$

$$= 8 \times 10^{-3} \text{ mol COOH/L water}$$

Chapter 1. Environmental Chemistry

1.1 Environmental composition: Solids

- Mass fraction of various kinds are used for solids without any ambiguity.

E.g. global avg. conc. of Fe: 4.1 wt%

V: 160 $\mu\text{g/g}$ = 160 ppm.

1.1 Environmental composition: Gases

- Molar fraction or percentage conc. (usu. mixing ratio) are used for gases. \propto vol. fraction \propto partial pressure
- For gases at low conc., 'parts per...' family of units is frequently used.
E.g. ppmv (parts per million by volume)
- Mass/vol, moles/vol, molecules/vol. are frequently used.
E.g. O_2 in air, mixing ratio = 20.95% = 9.35×10^{-3} mol/L = 0.299 g/L

Chapter 1. Environmental Chemistry

1.1 Environmental composition: Species distribution

- In many cases, the species distribution of the species, particularly existing in more than one form is more important.

E.g. carbonate species and mercury in water

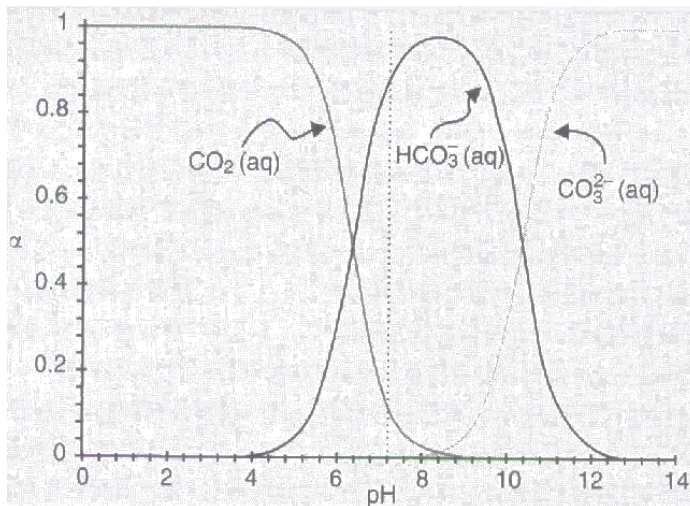


Fig. 1.2 Distribution of carbonate species as a function of pH. The α value is the fraction of a particular species; $\alpha = [\text{individual species}] / [\text{all species}]$.

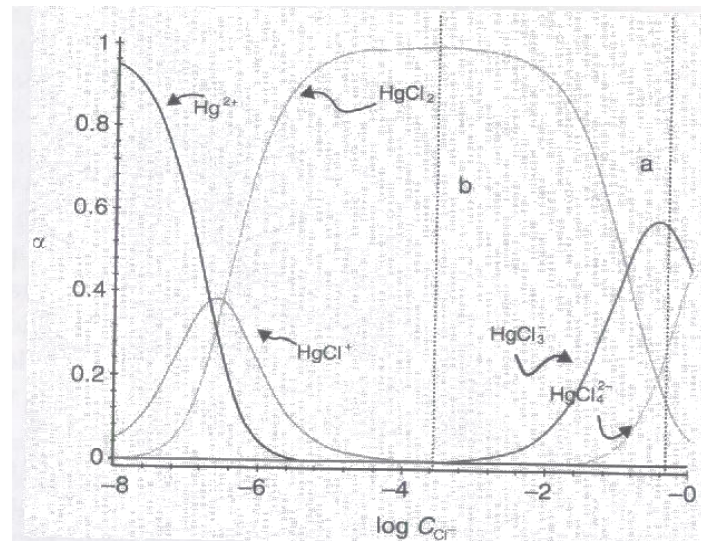


Fig. 1.3 Distribution of mercury chloro species in water as a function of chloride ion concentration, C_{Cl^-} (mol L^{-1}). The α value is the fraction of mercury in the form of a particular complex.

a: oceans with 0.56 mol/L Cl^- content

b: well water with 2.7×10^{-4} mol/L Cl^-

Chapter 1. Environmental Chemistry

1.2 Chemical Processes

• Four principal compartments of the environments

- The atmosphere (the gaseous environment)
- The hydrosphere (the liquid, essentially aqueous environment)
- The terrestrial (solid) environment
- The biosphere (the living environment)

E.g. Water cycle

Since all processes are at steady state, the residence time of water in the atmosphere can then be determined by

$$\begin{aligned}\tau &= \text{residence time} \\ &= \frac{\text{steady state amount in the atmosphere}}{\text{flux (in or out)}} \\ &= \frac{1.3 \times 10^{16} \text{ kg}}{4.96 \times 10^{17} \text{ kg y}^{-1}} \\ &= 0.0262 \text{ y} = 9.6 \text{ days}\end{aligned}$$

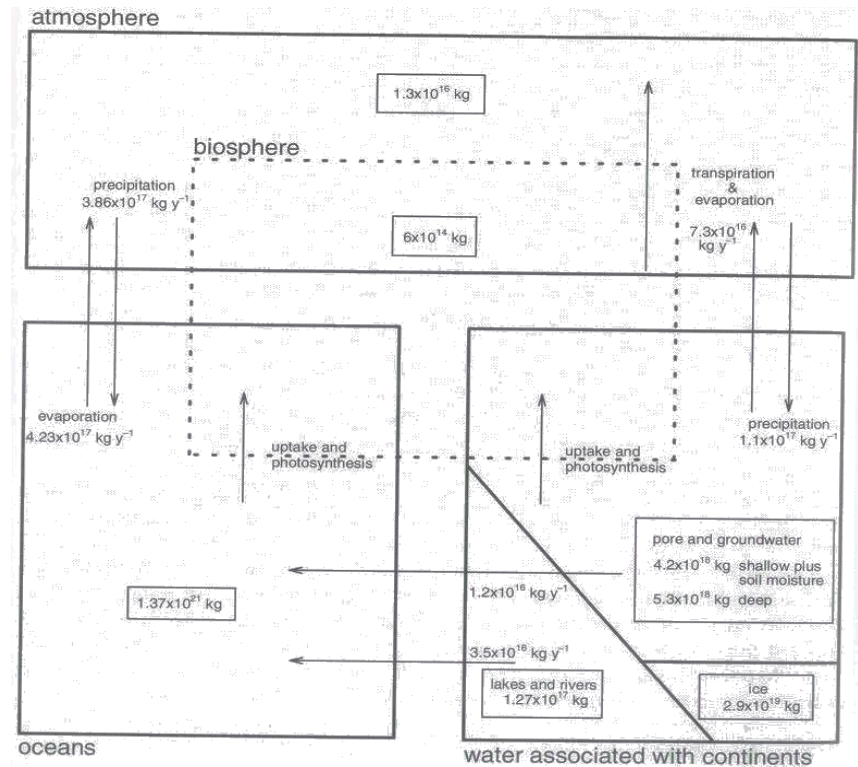


Fig. 1.4 The water cycle. Boxed values in kg are total amounts in the given compartment. Values in kg y^{-1} are fluxes or movement from one compartment to another. (Values taken from a number of sources and reported in Berner, E. K. and R. A. Berner, *The Global Water Cycle*, Prentice Hall, Inc., NJ, 1987.)

Chapter 1. Environmental Chemistry

1.3 Anthropogenic (human) effects

- Human activity effects on the natural processes

E.g. The Bhopal disaster in India (3 December, 1984)

- massive release of methyl isocyanate ($\text{CH}_3\text{-N=C=O}$) gas from the storage tank
- killed 3,000 persons, 300,000 persons affected by exposure
- MIC is a starting material for carbaryl that is carbamate pesticide
- Usu. stored under refrigeration in an underground
- Causes: technological problems (T) + human activity factors (H)

T: failure of cooling unit, leakage of water into the tank, loss of nitrogen pressure above the MIC, failure of safety device, etc.

H: political, organizational, and human factors, etc.

Part 1. The Earth's Atmosphere

Chapter 2. The Earth's Atmosphere

Chapter 2. The earth's atmosphere

2.1 Regions of the atmosphere: General Introduction

- Major components: following mixing ratios are const. up to an altitude of ab. 80 km due to the kinetic energy of gas molecules, being sufficiently big enough to overcome any gravitational forces

Table 2.1 Major components of the atmosphere near the surface of the Earth

Component	Mixing ratio
Nitrogen	78.08%
Oxygen	20.95%
Argon	0.93%
Carbon dioxide	0.0365%

Mixing ratios are calculated on a dry atmosphere basis. The water content is a fifth major component, but its concentration is variable, ranging from 0.5 to 3.5%.

Avg. molar mass of the atmosphere, \overline{M}_a

$$\begin{aligned}\overline{M}_a &= M_{N_2} \times f_{N_2} + M_{O_2} \times f_{O_2} + M_{Ar} \times f_{Ar} + M_{CO_2} \times f_{CO_2} \\ &= 28.96 \text{ gmol}^{-1}\end{aligned}$$

Total mass of the atmosphere

$$M_{atm} = \frac{P^0 4\pi r^2}{g} \text{ [in kg]}$$

$$= 5.27 \times 10^{18} \text{ kg}$$

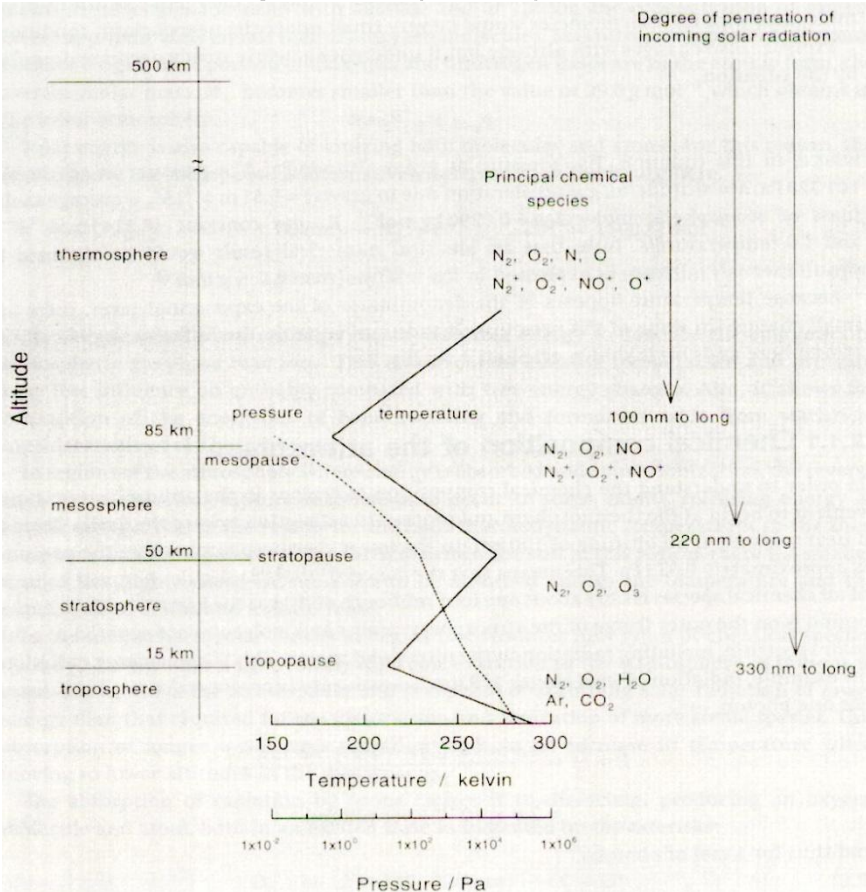
$$P^0 = 101325 \text{ Pa}, g = 9.81 \text{ ms}^{-2}$$

$$r = 6.37 \times 10^6 \text{ m (radius of the Earth)}$$

Chapter 2. The earth's atmosphere

2.1 Regions of the atmosphere: General Introduction

- Four sections of the atmosphere: depending on the T change direction, troposphere (대류권), stratosphere (성층권), mesosphere (중간층), thermosphere (열권)



Pressure changes with altitude

$$P_h = P^0 e^{-\bar{M}_a gh / RT}$$

h=altitude in meter

P_h =pressure at given altitude in Pa

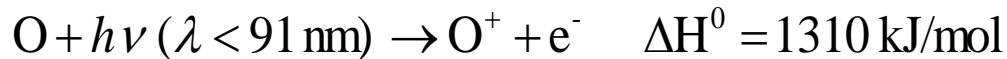
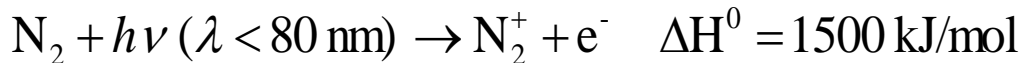
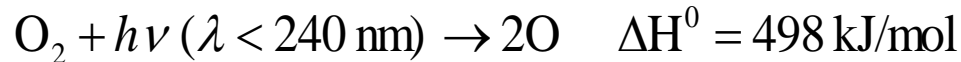
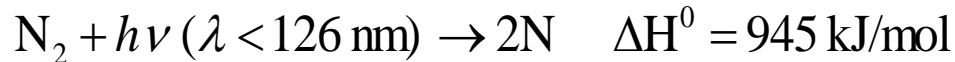
Chapter 2. The earth's atmosphere

2.1 Regions of the atmosphere: Chemical composition

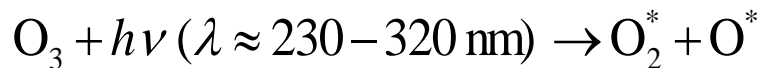
- In thermosphere (열권) : nearly vacuum at ab. the altitude of 100 km

- For one photon,
$$E = \frac{hc}{\lambda} = \frac{6.6 \times 10^{-34} \text{ Js} \times 3.0 \times 10^8 \text{ ms}^{-1}}{100 \times 10^{-9} \text{ m}}$$
$$= 2.0 \times 10^{-18} \text{ J/photon}$$

- For 1 mol of photons, $E = 2.0 \times 10^{-18} \times 6.0 \times 10^{23} = 1200 \text{ kJ/mol}$



- In mesosphere (중간층): some amount of O_3 that absorbs solar radiation



Chapter 2. The earth's atmosphere

2.1 Regions of the atmosphere: The troposphere

- Convection currents and winds cause constant movement of the air

Location	Atmospheric characteristic
Oceans	Sea salt aerosol (sodium, calcium, magnesium, chloride, sulfate)
Land (dry)	Airborne dust (soil related, plant pollens, etc.)
Urban	High levels of pollutants (smoke, dust, primary and secondary smog chemicals)
Arid tropics	Low humidity, intense solar radiation
Humid tropics	High humidity, natural volatile organics, intense solar radiation
Arctic	Sunlight period variable on a yearly cycle, Arctic haze (including sulfate aerosols, soot, and metals)

Chapter 2. The earth's atmosphere

2.2 Reactions and calculations in atmospheric chemistry:

Thermodynamic calculations

- For $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
- At 25 °C, $\Delta G^0 = 2\Delta G_f^0 = 2 \times (+86.55) = +173.1 \text{ kJ/mol}$ uneasy reaction at R.T.
- At 1500 °C (I.e. in a cylinder of an internal combustion engine at the time of ignition), $\Delta G_{2773}^0 = 2\Delta H_{f(\text{NO})}^0 - T(2S_{\text{NO}}^0 - S_{\text{N}_2}^0 - S_{\text{O}_2}^0) = 111.2 \text{ kJ/mol}$

- Then the equilibrium constant is

$$\ln K_P = \frac{-\Delta G_T^0}{RT} = \frac{-111200 \text{ J/mol}}{8.314 \text{ J/mol/K} \times 2773 \text{ K}} = -4.82 \therefore K_P = 0.0080$$

- Since $K_P = \frac{(P_{\text{NO}}/P^0)^2}{(P_{\text{N}_2}/P^0)(P_{\text{O}_2}/P^0)}$ if after complete burning, $P_{\text{N}_2} = 650 \text{ kPa}$, $P_{\text{O}_2} = 1.0 \text{ kPa}$ in the compressed cylinder gas at 2500 °C, then after some reaction between O_2 and N_2 (meaning the loss of partial pressure, x , of each)

- $\frac{4x^2}{(650-x)(1.0-x)} = 0.0080$ if $x \ll 650 \text{ kPa}$, then $4x^2 + 5.2x - 5.2 = 0 \therefore x = 0.66$

- Therefore, $P_{\text{NO}} = 2x = 1.4 \text{ kPa}$ I.e. NO ratio in hot cylinder = $\frac{1.4 \text{ kPa}}{650 \text{ kPa}} \times 10^6 \text{ ppmv} = 2200 \text{ ppmv}$

Chapter 2. The earth's atmosphere

2.2 Reactions and calculations in atmospheric chemistry:

Kinetic calculations

- For the reverse reaction of $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$ $k_2 = 2.6 \times 10^6 e^{-3.21 \times 10^4 / T} \text{ m}^3 / \text{mol/s}$
- At 25 °C, $k_2 = 4.3 \times 10^{-41} \text{ m}^3 / \text{mol/s}$ if atmospheric conc. of NO=100 ppbv
- Then the initial rate of decomposition of NO at R.T. is

$$k_2[\text{NO}]_i^2 = 7.2 \times 10^{-52} \text{ mol/m}^3 / \text{s}$$

- The half-life, $t_{1/2} = \frac{1}{k_2[\text{NO}]_i} = 1.8 \times 10^{38} \text{ y}$: 10^{28} times longer than the age of the Earth
- This means there should be other reactions must be involved in controlling the atmospheric conc. of NO -> **Think what?**

Chapter 2. The earth's atmosphere

2.2 Reactions and calculations in atmospheric chemistry:

Photochemical reactions

- For $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$ reaction rate = $f_1[\text{NO}_2]$
- Since the production rxn = consumption rxn, $k_2[\text{ROO}\cdot][\text{NO}] = f_1[\text{NO}_2]$
- Therefore $\frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_2[\text{ROO}\cdot]}{f_1}$

2.2 Reactions and calculations in atmospheric chemistry:

Reactions involving free radicals

