Environmental Chemistry

Part 2 Atmospheric Chemistry

2.2 Atmospheric Composition

Composition of the atmosphere

Gas	% by volume	
N_2	78.08	
O_2	20.95	
Ar	0.93	Dry air
CO_2	0.03	
All other gases (Ne, He, Kr, H, etc)	0.01	
Water	Variable	

Water vapor in the air

- The % volume of Water vapor is variable, depending on temperature, precipitation, rate of evaporation and other factors at a particular location.
- The percentage of water vapor ranges from 0.1-5%. Generally it is 1-3% (the 3rd most abundant constituents in the air).

Expressing the amount of substances in the atmosphere

- Concentration
  – the amount (mass, moles, molecules, etc) of a substance in a given volume divided by that volume.
  – The example concentration units are mg/m^3, mol/m^3, molecules/cc, and etc.
- Mixing ratio
  – the ratio of the amount of the substance in a given volume to the total amount of all constituents in that volume.

Mixing Ratio

$$\zeta_i = \frac{n_i}{n_{total}}$$

n_i is the molar concentration of i and n_{total} is the total molar concentration of air.

parts per million (ppm)	10^{-6}	$\mu mol\ mol^{-1}$
parts per billion (ppb)	10^{-9}	$nmol\ mol^{-1}$
parts per trillion (ppt)	10^{-12}	$pmol\ mol^{-1}$

$$\zeta_i(ppm) = 10^6 x \frac{n_i}{n_{total}}$$

Conversion between ppm and μg/m³

$$n_i = \frac{10^{-6} m_i}{M_i}$$

n_i: mol/m³
m_i: μg/m³
M_i: g/mol

$$n_{total} = \frac{N}{V} = \frac{P}{RT}$$

$$mixing\_ratio\_in\_ppm = 10^6 \frac{n_i}{n_{total}}$$

$$= 10^6 \frac{10^{-6} \frac{m_i}{M_i}}{\frac{p}{RT}} = \frac{RT}{pM_i} m_i$$

$$mixing\_ratio\_in\_ppm = \frac{RT}{pM_i} x Concentration\_in\_\mu g / m^3$$

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Pressure unit and R Constant:

P= 1.01325x10^5 pascal

R= 8.314 J/k.mol for P in Pa and volume in m^3

Conversion between ppm and μg/m³

Example:

The Hong Kong Air Quality Objective for ozone is 240 μg/m³. The U.S. National Ambient Air Quality Standard for ozone is 120 ppb. Which standard is stricter at the same temperature (25°C) and the pressure (1atm)?

$$mixing\_ratio\_in\_ppm = \frac{8.314x298}{1.01325x10^5 x48} x240 \mu g/m^3 = 0.122\,ppm = 122\,ppb$$

Typical mixing ratios for some compounds of environmental importance

Carbon dioxide	355 ppm
Carbon monoxide	100 ppb to 20 ppm
Ozone	1 to 100 ppb
Methane	1.72 ppm
Nonmethane hydrocarbon	1 ppt to < 1 ppb
Nitric oxide (NO)	5 ppt to 1 ppb
Nitrogen dioxide (NO2)	1 to 150 ppb
Nitrous oxide (N2O)	310 ppb
Sulfur dioxide	1 to 100 ppb
CFCl3 (Freon 11)	200 ppt
CF2Cl2 (Freon 12)	350 ppt

ppm in solution vs. ppm as mixing ratio for airborne substances

ppm: Parts per million

solution

$$C_i(ppm) = \frac{weight\_of\_Species\_i}{weight\_of\_solution} x10^6$$

air

$$\zeta_i = \frac{mole\_of\_species\_i}{mole\_of\_air\_molecules}$$

$$density\_of\_dilute\_aqueous\_solution \approx density\_of\_water$$
$$= 1g/ml = 10^3 g/liter = 10^6 mg/L$$

$$1\_ppm = \frac{1mg\_species\_i}{10^6 mg\_solution}$$
$$= \frac{1mg}{1\_liter\_solution} = 1mg/L$$

Relative Humidity

Definition: ratio of the partial pressure of water to its saturation vapor pressure at the same temperature.

$$\mathrm{RH} = 100\,\frac{P_{H_2O}}{P^{o}_{H_2O}}$$

$$\mathrm{RH} = 100\,\frac{y}{y_s}$$

y: mole fraction of water vapor at temperature T

y_s: mole fraction of saturation water vapor at Temperature T

Relative Humidity

Calculation of H_2O mixing ratio in ppm from RH

$$\mathrm{RH} = 100\frac{y}{y_s}$$

$$[H_2O] = 10^6 y = 10^4 RHy_s (ppm)$$

$$[H_2O] = 10^4 RH\frac{P^o_{H_2O}}{p}(ppm)$$

$p^o_{H_2O}$ = p exp[13.3185a - 1.976 a^2 - 0.6445 a^3 -0.1299 a^4]

where p = 1 atm and a = 1-(373.15/T).

Hong Kong Air Quality Objectives (HKAQO) μg/m^3

Air Pollutants	1-hour	8-hour	24-hour	3-month	1-year
Sulphur dioxide	800	--	350	--	80
Nitrogen dioxide	300	--	150	--	80
Carbon monoxide	30000	10000	--	--	--
Ozone	240	--	--	--	--
Total suspended particulate	--	--	260	--	80
Respirable suspended particulates	--	--	180	--	55
Lead	--	--	--	1.5	--