Fundamental of Environmental Engineering

Chapter 2: Units of Concentration

Mass Concentration Units

Volume/Volume and Mole/Mole Units

Partial Pressure Units

Mole/Volume Units

Other Types of Units

1. Mass concentration Units

1.1 Mass/Mass Unit: ppm_m, mg/kg

$$ppm_m = \text{g of i in } 10^6 \text{ g total}$$

$$ppm_m = \frac{m_i}{m_{total}} \times 10^6$$

$$\frac{m_i}{m_{total}} = \text{mass fraction}$$

Similar definitions: ppb_m (part per billion), ppt_m (part per trillion)

Ex.1 A one-kg sample of soil contains 5 mg of trichloroethylene (TCE). What is the TCE concentration in ppm_m and ppb_m?

Solution

$$[TCE] = \frac{5\text{mgTCE}}{1\text{kgSoil}} = \frac{5\times10^{-3}\text{gTCE}}{10^{3}\text{gSoil}} = 5ppm_m = 5{,}000ppb_m$$

1.2 Mass/Volume Unit: mg/L, μg/L, mg/m^3, and $\mu g/m^3$

In most aqueous systems, ppm_m is equivalent to mg/L because the density of pure water is approximately 1,000 g/L.

<u>Ex.2</u> One liter of water contains 5 mg of trichloroethylene (TCE). What is the TCE concentration in mg/L and ppm_m?

<u>Solution</u>

$$[TCE] = \frac{5 mg TCE}{1 L H_2O} = \frac{5 mg}{L}$$

$$[TCE] = \frac{5 mg TCE}{1 L H_2O} \times \frac{1 L H_2O}{1{,}000 g H_2O} = \frac{5 \times 10^{-3} g TCE}{10^3 g H_2O} = 5 ppm_m$$

2. Volume/Volume and Mole/Mole Units

Units of volume fraction or mole fraction are frequently used for gas concentrations: ppm_v (part per million by volume)

$$ppm_v = \frac{V_i}{V_{total}} \times 10^6$$

$$\frac{V_i}{V_{total}} = \text{volume fraction}$$

The advantage of volume/volume units is that gaseous concentrations reported in these units do not change as a gas is compressed or expanded.

2.1 Using the Ideal Gas Law to Convert ppm_v to $\mu g/m^3$

Ideal Gas Law:

$$PV = nRT$$

where P = the pressure
V = the volume occupied
n = the number of moles
R = the gas constant
T = the absolute temperature

Homework: The gas constant, R, may be expressed in many different sets of units. Show at least 4 of them?

Solution

Such as

$$R = 8.205 \times 10^{-5} \frac{m^3 \cdot atm}{mole \cdot K}$$

The Ideal Gas Law states that “the volume occupied by a given number of molecules of any gas is the same, no matter what the molecular weight or composition of the gas, as long as the pressure and temperature are constant”:

$$V = n\frac{RT}{P}$$

Therefore, at standard conitions (P = 1 atm, T = 273.15 ^{o}C), one mole of any pure gas will occupy a volume of 22.4 L.

Ex.3 A gas mixture contains 0.001 mole of sulfur dioxide (SO_2) and 0.999 mole of air. What is the SO_2 concentration, expressed in units of ppm_v?

Solution

$$[SO_2] = \frac{V_{SO_2}}{V_{total}} \times 10^6$$

$$V_{SO_2} = 0.001\,\text{mole}\,SO_2 \times \frac{RT}{P}$$

$$V_{total} = (0.999 + 0.001)\ \text{mole total} \times \frac{RT}{P}$$

$$\therefore [SO_2] = \frac{0.001\,\text{mole}\,SO_2 \times \frac{RT}{P}}{(0.999 + 0.001)\ \text{mole total} \times \frac{RT}{P}} \times 10^6 = 1{,}000\ ppm_v$$

or

$$[SO_2] = \frac{\text{mole}_{SO_2}}{\text{mole}_{total}} \times 10^6 = \frac{0.001\,\text{mole}\,SO_2}{(0.999 + 0.001)\ \text{mole total}} \times 10^6 = 1{,}000\ ppm_v$$

From Ex.3, it can be seen that:

$$ppm_v = \frac{V_i}{V_{total}} \times 10^6 = \frac{\text{mole}_i}{\text{mole}_{total}} \times 10^6$$

Ex.4 The SO_2 concentration is 100 ppb_v. What is the concentration in the unit of μg/m³? Assume the temperature is 28 °C and pressure is 1 atm.

Solution

$$100ppb_v = \frac{100\ m^3SO_2}{10^9\ m^3Air}$$

First, convert the volume of SO_2 to a number of mole

$$\frac{100\ m^3SO_2 \times \frac{P}{RT}}{10^9\ m^3Air} = \frac{100\ m^3SO_2 \times \frac{1atm}{\left(8.205\times10^{-5}\frac{m^3\cdot atm}{mole\cdot K}\right)(301K)}}{10^9\ m^3Air} = \frac{4.05\times10^{-6}\ moleSO_2}{m^3Air}$$

Then, convert the moles of SO_2 to mass

$$= \frac{4.05\times10^{-6}\ moleSO_2}{m^3Air} \times \frac{64gSO_2}{moleSO_2} \times \frac{10^6\mu g}{g} = \frac{260\mu g}{m^3}$$

3. Partial-Pressure Units

From the Ideal Gas Law, at the given temperature and volume, pressure is directly proportional to the number of moles of gas present; therefore, pressure fractions are identical to mole fractions (and volume fractions). For this reason, partial pressure (P_i) can be calculated as the product of the mole or volume fraction and the total pressure as shown:

$$P_i = (\text{volume fraction or mole fraction}) \times P_{total}$$
$$= (ppm_v \times 10^{-6}) \times P_{total}$$

$$ppm_v = \frac{P_i}{P_{total}} \times 10^{-6}$$

So far, we know:

$$ppm_v = \frac{V_i}{V_{total}} \times 10^6 = \frac{mole_i}{mole_{total}} \times 10^6 = \frac{P_i}{P_{total}} \times 10^6$$

Ex.5 The concentration of gas-phase polychlorinated biphenyls (PCBs) above Lake Superior is 450 picograms per cubic meter (pg/m³). What is the partial pressure (in atm) of PCBs? Assume the temperature is 0°C, the atmospheric pressure is 1 atm, and the average molecular weight of PCBs is 325.

Solution

First, find the number of moles of PCBs in a liter of air.

$$450 \frac{pg}{m^3 air} \times \frac{mole}{325g} \times 10^{-12} \frac{g}{pg} \times 10^{-3} \frac{m^3}{L} = 1.38 \times 10^{-15} \frac{mole\ PCBs}{L\ air}$$

Then, find mole fraction using the ideal gas law

$$1.38 \times 10^{-15} \frac{mole\ PCBs}{L\ air} \times \frac{22.4L\ air}{mole\ air} = 3.1 \times 10^{-14} \frac{mole\ PCBs}{mole\ air}$$

Find the partial pressure

$$P_{PCBs} = 3.1 \times 10^{-14} \times 1\,atm = 3.1 \times 10^{-14}\,atm$$

Table 2-2. Composition of the Atmosphere*

Compound	Concentration (% volume or moles)	Concentration (ppm_V)
Nitrogen (N_2)	78.1	781,000
Oxygen (O_2)	20.9	209,000
Argon (Ar)	0.93	9,300
Carbon dioxide (CO_2)	0.035	350
Neon (Ne)	0.0018	18
Helium (He)	0.0005	5
Methane (CH_4)	0.00017	1.7
Krypton (Kr)	0.00011	1.1
Hydrogen (H_2)	0.00005	0.500
Nitrous oxide (N_2O)	0.000032	0.316
Ozone (O_3)	0.000002	0.020

Data from Graedel and Crutzen, 1993.

*Values represent concentrations in dry air at remote locations.

3.1 Corrected Partial-Pressure for Moisture

Ex.6 What would be the partial pressure (in atm) of carbon dioxide (CO_2) when the barometer reads 101.325 kPa, the relative humidity is 80%, and the temperature is 20°C? The concentration of CO_2 in dry air is 350 ppm_v.

Solution

The total pressure must first be corrected for the moisture present in the air.

$$P_{total} - P_{water} = 101.325 - 2.34 \times 0.8 = 99.453\,\text{kPa}$$

The partial pressure of CO_2 would be

$$P_{CO_2} = \text{volume fraction} \times \text{corrected } P_{total}$$

$$= 350\text{ppm}_v \times \frac{10^{-6}\,\text{volume fraction}}{\text{ppm}_v} \times \left[99.453\text{kPa} \times \frac{1\text{atm}}{101.325\text{kPa}}\right] = 3.4 \times 10^{-4}\,\text{atm}$$

TABLE C-2

Physical properties of water (SI units)[a]

Temperature, °C	Specific weight, γ, kN/m^3	Density,[b] ρ, kg/m^3	Modulus of elasticity,[b] $E/10^6$, kN/m^2	Dynamic viscosity, $\mu \times 10^3$, N · s/m^2	Kinematic viscosity, $\nu \times 10^6$, m^2/s	Surface tension,[c] σ, N/m	Vapor pressure, p_v, kN/m^2
0	9.805	999.8	1.98	1.781	1.785	0.0765	0.61
5	9.807	1000.0	2.05	1.518	1.519	0.0749	0.87
10	9.804	999.7	2.10	1.307	1.306	0.0742	1.23
15	9.798	999.1	2.15	1.139	1.139	0.0735	1.70
20	9.789	998.2	2.17	1.002	1.003	0.0728	2.34
25	9.777	997.0	2.22	0.890	0.893	0.0720	3.17
30	9.764	995.7	2.25	0.798	0.800	0.0712	4.24
40	9.730	992.2	2.28	0.653	0.658	0.0696	7.38
50	9.689	988.0	2.29	0.547	0.553	0.0679	12.33
60	9.642	983.2	2.28	0.466	0.474	0.0662	19.92
70	9.589	977.8	2.25	0.404	0.413	0.0644	31.16
80	9.530	971.8	2.20	0.354	0.364	0.0626	47.34
90	9.466	965.3	2.14	0.315	0.326	0.0608	70.10
100	9.399	958.4	2.07	0.282	0.294	0.0589	101.33

[a] Adapted from Ref. 2.

[b] At atmospheric pressure.

[c] In contact with air.

Relative humidity - the ratio of the amount of water in the air at a give temperature to the maximum amount it could hold at that temperature; expressed as a percentage

Water vapor - water in a vaporous form diffused in the atmosphere but below boiling temperature

Vapor pressure - the pressure exerted by a vapor; often understood to mean saturated vapor pressure (the vapor pressure of a vapor in contact with its liquid form)

Viscosity - A property of a fluid that characterizes its perceived “thickness” or resistance to pouring. It describes a fluid’s internal resistance to flow and may be thought of as a measure of fluid friction. Thus, methanol is thin, having a low viscosity, while vegetable oil is thick having a high viscosity.

Modulus of elasticity - (physics) the ratio of the applied stress to the change in shape of an elastic body

4. Mole/Volume Units

Molarity (M) (the unit called “molar”) : the number of moles of a solute per one liter of solution.

Don’t be confused with molality (m) (the unit called “molal”) : the number of moles of a solute added to exactly one liter of solvent.

Ex.7 The concentration of trichloroethene (TCE) is 5 mg/L. What is the concentration of TCE in units of molarity? The molecular weight of TCE is 131.5 g/mole.

Solution

$$\frac{5\text{mgTCE}}{\text{L}} \times \frac{1\text{g}}{10^3\text{mg}} \times \frac{1\text{mole}}{131.5\text{g}} = 3.8 \times 10^{-5}\text{M}$$

5. Other Types of Units

5.1 Normality (N, equivalents/L):
Mostly used in acid/base or oxidation/reduction reactions

"Reporting concentration on an equivalent basis is useful because if two chemical species react and the two species reacting have the same strength on an equivalent basis, a 1-mL volume of reactant number 1 will react with a 1-mL volume of reactant number 2".

For example, HCl, H_2SO_4 and H_3PO_4 have 1, 2 and 3 equivalents/mole of H^+ that the acid can potentially donate, respectively.

Ex.8 What is the equivalent weight of HCl, H_2SO_4, NaOH, $CaCO_3$, and aqueous CO_2?

Solution

The equivalent weight is found by dividing the molecular weight by the number of equivalents.

$$\text{eqv wt of HCl} = \frac{1+35.5\text{g}}{\text{mole}} \div \frac{1\,\text{eqv}}{\text{mole}} = \frac{36.5\text{g}}{\text{eqv}}$$

$$\text{eqv wt of } H_2SO_4 = \frac{(2\times1)+32+(4\times16)\text{g}}{\text{mole}} \div \frac{2\,\text{eqv}}{\text{mole}} = \frac{49\text{g}}{\text{eqv}}$$

$$\text{eqv wt of NaOH} = \frac{23+16+1\text{g}}{\text{mole}} \div \frac{1\,\text{eqv}}{\text{mole}} = \frac{40\text{g}}{\text{eqv}}$$

$$\text{eqv wt of } CaCO_3 = \frac{40+12+(3\times16)\text{g}}{\text{mole}} \div \frac{2\,\text{eqv}}{\text{mole}} = \frac{50\text{g}}{\text{eqv}}$$

Aqueous carbon dioxide is not an acid until it hydrates in water and forms carbonic acid

$$(CO_2 + H_2O \rightarrow H_2CO_3) = \frac{12+(2\times16)\text{g}}{\text{mole}} \div \frac{2\,\text{eqv}}{\text{mole}} = \frac{22\text{g}}{\text{eqv}}$$

Ex.8 What is the normality of 1 M solutions of HCl, and H_2SO_4?

Solution

$$1\,\text{M HCl} = \frac{1\text{mole}\,\text{HCl}}{\text{L}} \times \frac{1\,\text{eqv}}{\text{mole}} = \frac{1\,\text{eqv}}{\text{L}} = 1\,\text{N}$$

$$1\,\text{M } H_2SO_4 = \frac{1\text{mole}\,H_2SO_4}{\text{L}} \times \frac{2\,\text{eqv}}{\text{mole}} = \frac{2\,\text{eqv}}{\text{L}} = 2\,\text{N}$$

Note that on an equivalent basis, a 1-M solution of sulfuric acid is twice as strong as a 1-M solution of HCl.

Homework: A chemical analysis of the mineral water resulted in the following cations and anions being identified with corresponding concentrations (mg/L): $[Ca^{2+}]$ = 2.9; $[Mg^{2+}]$ = 2.0; $[Na^{+}]$ = 11.5; $[K^{+}]$ = 3.3; $[HCO_3^-]$ = 40; $[SO_4^{2-}]$ = 4.7; $[F^-]$ = 0.09; $[Cl^-]$ = 7.7

Is the analysis correct? Hint: All aqueous solutions must maintain charge neutrality

5.2 Concentration as a Common Constituent

EXAMPLE 2.13. CONCENTRATIONS AS A COMMON CONSTITUENT

A water contains two nitrogen species. The concentration of NH_3 is 30 mg/L NH_3 and the concentration of NO_3^- is 5 mg/L NO_3^-. What is the total nitrogen concentration in units of mg N/L?

SOLUTION

Use the appropriate molecular weight and stoichiometry to convert each individual species to the requested units of mg N/L, then add the contribution of each species.

$$\frac{30 \text{ mg } NH_3}{\text{L}} \times \frac{\text{mole } NH_3}{17 \text{ g}} \times \frac{\text{mole N}}{\text{mole } NH_3} \times \frac{14 \text{ g}}{\text{mole N}} = \frac{24.7 \text{ mg } NH_3\text{-N}}{\text{L}}$$

$$\frac{5 \text{ mg } NO_3^-}{\text{L}} \times \frac{\text{mole } NO_3^-}{62 \text{ g}} \times \frac{\text{mole N}}{\text{mole } NO_3^-} \times \frac{14 \text{ g}}{\text{mole N}} = \frac{1.1 \text{ mg } NO_3^-\text{-N}}{\text{L}}$$

$$\text{Total nitrogen concentration} = 24.7 + 1.1 = \frac{25.8 \text{ mg N}}{\text{L}}$$

EXAMPLE 2.14. DETERMINATION OF A WATER'S HARDNESS

Water has the following chemical composition. $[Ca^{2+}]$ = 15 mg/L; $[Mg^{2+}]$ = 10 mg/L; $[SO_4^{2-}]$ = 30 mg/L. What is the total hardness in units of mg/L as $CaCO_3$?

SOLUTION

Find the contribution of hardness from each divalent cation. Anions and all non-divalent cations are not included in the calculation.

$$\frac{15 \text{ mg } Ca^{2+}}{L} \times \left(\frac{\frac{50 \text{ g } CaCO_3}{\text{eqv}}}{\frac{40 \text{ g } Ca^{2+}}{2 \text{ eqv}}} \right) = \frac{38 \text{ mg}}{L} \text{ as } CaCO_3$$

$$\frac{10 \text{ mg } Mg^{2+}}{L} \times \left(\frac{\frac{50 \text{ g } CaCO_3}{\text{eqv}}}{\frac{24 \text{ g } Mg^{2+}}{2 \text{ eqv}}} \right) = \frac{42 \text{ mg}}{L} \text{ as } CaCO_3$$

Therefore, the total hardness is 38 + 42 = 80 mg/L as $CaCO_3$. Note this water is moderately hard. Also, note that if reduced iron (Fe^{2+}) or manganese (Mn^{2+}) were present, they would be included in the hardness calculation.

Table 2-4. Range of Concentrations Encountered in Natural Waters

Substance	Rain, Fog	Lakes, Rivers	Groundwater	Oceans
Trace metals (e.g., Pb, Cu, Hg, Zn)	0.01–100 μg/L	0.001–10 μg/L	0.1–10^6 ng/L	0.01–100 ng/L
Organic pollutants (e.g., PCBs, pesticides, solvents)	1–5,000 ng/L	0.1–500 ng/L	0.001–10^6 ng/L	0.001–10 pg/L
Major ions				
Ca^{2+}	0.1–20 mg/L	1–120 mg/L	1–120 mg/L	800 mg/L
Cl^-	0.05–10 mg/L	0.1–30 mg/L	0.1–50 mg/L	35,000 mg/L

Table 2-5. Arsenic Concentrations in Southern California's Central and West Basin Groundwater Supplies

Groundwater Basin	Number Wells Tested	Number of Wells with Arsenic, Four Ranges			
		<0.5 μg/L	0.5–1.9 μg/L	2–5 μg/L	>5 μg/L
Central	227	13	58	119	37
West	35	14	19	1	1

Adapted from Ried, 1994.

Table 2-6. Dry Weather Leachate Concentration from the Goff Mountain Landfill, West Virginia

Parameter	Range (mg/L)	Average (mg/L)
Chemical oxygen demand (COD)	4,500–8,310	7,090
Total organic carbon (TOC)	169–2,820	1,270
Total suspended solids (TSS)	130–189	160
Volatile suspended solids (VSS)	108–149	120
NH_3-N	—	296
PO_4^{3-}-P	—	Below analytical detection
Alkalinity (as mg/L $CaCO_3$)	—	1,420

Adapted from Campbell et al., 1995.