## CHAPTER SEVEN: MEASURES OF POLLUTION

### 7.1 The Problem

Pollutants come in many physical and chemical forms, and almost always as a mixture. There will be dissolved chemicals in water, particles in liquids and gases, solids mixed with other solids, and gases mixed with air. The pollutants need to be identified and quantified as the first step in defining the problem. Then concentrations, volume flow rates, and mass flow rates are needed to solve the problem. This chapter reviews common units that are used to measure concentration, volume, mass, and flow rate. It will also define some measures of pollution.

### 7.2 Pollutants

### 7.2.1 Classes of Pollutants

Toxic and hazardous chemicals, such as benzene, copper and other heavy metals, pesticides, and other organic chemicals, are specifically identified and given limits in the regulations. These must be measured individually as specific chemicals. 'Lumped' characteristics are commonly used for solids and organics in wastewater, including particulate matter (PM), suspended solids (SS), total dissolved solids (TDS), and chemical oxygen demand (COD). In water the particles may be organic or inorganic, biological (bacteria and algae), or chemical. Particulate matter (PM) in air measures the total concentration or total mass and does not differentiate the kinds of solids, such as metal fumes, fly ash, dust or pollen in air.

### 7.2.2 Solids in Water and Wastewater

Solids in water and wastewater are measured as mass per volume, usually $\mathrm{mg} / \mathrm{L}$. In many applications it is sufficient to use 'lumped' or aggregate measures, such as total solids, total volatile solids (organic solids), and total fixed solids (inert solids). These measures give no information about composition of the individual solid particles. Specific dissolved ions and dissolved organic compounds are unknown.

Total solids are the residue left in a vessel after the sample has been dried to a constant weight at $103-105^{\circ} \mathrm{C}$. Total solids include particles and dissolved materials. Volatile solids are measured as the mass of material that will burn off at $550^{\circ} \mathrm{C}$. Fixed solids are whatever will not burn at a temperature of $550^{\circ} \mathrm{C}$; fixed solids are the ash. Volatile solids are an aggregate measure of all the organic matter in a sample. All carbohydrates, fats, proteins, and synthetic chemicals will be measured as volatile solids. When a biological treatment process reduces the mass of total solids, the lost mass is volatile solids that have been converted to gas (usually methane or carbon dioxide). If the volatile solids decrease and fixed solids increase it is because organic compounds have been mineralized.

Suspended solids are particles that can be captured on a filter of $2.0 \mu \mathrm{~m}$ (or smaller) pore size. "Dissolved solids" pass through the filter. More correctly these are called filterable solids because this fraction includes very small particles (colloids) as well as truly dissolved chemicals. Dissolved solids could be measured by using filters with a finer pore size, or by using an ultra-centrifuge to remove the particles. The distinction between filterable solids and dissolved solids is unimportant in most applications and we will use dissolved solids. The relations are

Total solids $(T S)=$ Volatile solids $(V S)+$ Fixed solids $(F S)$
Total solids $(T S)=$ Total suspended solids (TSS) + Total dissolved solids (TDS)
Total suspended solids (TSS) = Volatile suspended solids (VSS) + Fixed suspended solids (FSS)
Total dissolved solids $(T D S)=$ Volatile dissolved solids $(V D S)+$ Fixed dissolved solids (FDS)

## Example 7.1 Relations Of Solids In Water And Wastewater

Figure 1.1 shows a possible distribution of solids in wastewater, but not necessarily a typical distribution. The objective is to define the classes of solids that are commonly measured to characterize wastewater.

$$
\begin{aligned}
& T D S=V D S+F D S=300 \mathrm{mg} / L+700 \mathrm{mg} / L=1,000 \mathrm{mg} / L \\
& T S S=V S S+F S S=100 \mathrm{mg} / L+100 \mathrm{mg} / L=200 \mathrm{mg} / L \\
& F S=F D S+F S S=700 \mathrm{mg} / L+100 \mathrm{mg} / L=800 \mathrm{mg} / L \\
& V S=V D S+V S S=300 \mathrm{mg} / L+100 \mathrm{mg} / L=400 \mathrm{mg} / L \\
& T S=V S+F S=400 \mathrm{mg} / L+800 \mathrm{mg} / L=1,200 \mathrm{mg} / L
\end{aligned}
$$

$\mathrm{TS}=400+800 \mathrm{mg} / \mathrm{L}=1,200 \mathrm{mg} / \mathrm{L}$


Figure 1.1 The relations of the different classes of solids that are commonly used to characterize wastewater

### 7.2.3 Biochemical Oxygen Demand (BOD)

There are no specific limits for carbohydrates, fats and proteins, or for the individual kinds of carbohydrates (glucose, starch, etc.) or for proteins and their amino acid building blocks (glycine, tryptophan, etc.). There are regulations for aggregates of these kinds of organic chemicals. What they have in common is that they can be decomposed and metabolized by bacteria and other microbes. Almost all wastewater treatment plants include processes to accomplish this biodegradation under controlled conditions.

Biochemical Oxygen Demand (BOD) is a measure of the oxygen consuming activity of aerobic (i.e, oxygen consuming) microorganisms. Oxygen consumption is proportional to the amount biodegradable organic compounds that are metabolized by the organisms as they consume the oxygen.

Every wastewater treatment plant has an effluent limit for BOD, which may range from $5 \mathrm{mg} / \mathrm{L}$ to $30 \mathrm{mg} / \mathrm{L}$ (in the U.S.). Whatever portion of influent BOD that is not eliminated in the treatment process can be exerted in a lake or stream, thus reducing the dissolved oxygen that is needed for a healthy aquatic population.

The 5-day BOD test is a bioassay that is done in sealed bottles (BOD bottles) that contain diluted wastewater. The dilution water-wastewater mixture is aerated to give an initial dissolved oxygen (DO) concentration close to $9 \mathrm{mg} / \mathrm{L}$. (The saturation concentration of oxygen in clean water is $9.18 \mathrm{mg} / \mathrm{L}$ at $20^{\circ} \mathrm{C}$ ). The samples are
incubated at a standard temperature of $20^{\circ} \mathrm{C}$ for 5 days to measure the 5 -day $B O D$, or $B O D_{5}$. The dissolved oxygen concentration is measured after 5 days of incubation at a standard temperature of $20^{\circ} \mathrm{C}$.

The DO depletion ( $\Delta D O_{\text {bottle }}$ ) from the initial to the final concentration is proportional to the amount of biodegradable organic matter in the sample. The BOD of the bottle contents is

$$
B O D_{\text {bottle }}=\Delta D O_{\text {bottle }}=[\text { initial DO] }-[\text { final DO }]
$$

The final DO must be $2 \mathrm{mg} / \mathrm{L}$ or greater for the measurement to be valid. The DO depletion in the bottle must be less than $6-7 \mathrm{mg} / \mathrm{L}$. This requirement is the reason for incubating a diluted mixture.

The dilution factor $(D F)$ is the ratio of the BOD bottle volume to the volume of wastewater in the bottle.

$$
D F=\frac{\left(V_{\text {bottle }}\right)}{\left(V_{\text {sample }}\right)}
$$

$D F=30$ means a 10 mL wastewater volume in a 300 mL bottle; $D F=300 / 10$. $D F=2$ means that the incubated mixture is $50 \%$ effluent and $50 \%$ dilution water: $D F=300 / 150$.

The BOD of the undiluted wastewater is

$$
B O D_{\text {waste }}=(D O \text { depletion })\left(\frac{V_{\text {bottle }}}{V_{\text {sample }}}\right)=(\Delta D O)(D F)
$$

The effluent from a well-operated modern activated sludge process will be less than $10 \mathrm{mg} / \mathrm{L} \mathrm{BOD}_{5}$. A dilution factor of 2 should be suitable. $\mathrm{A} \mathrm{BOD}_{5}$ concentration of $200 \mathrm{mg} / \mathrm{L}$ to $300 \mathrm{mg} / \mathrm{L}$ is typical for municipal wastewater. A dilution factor $(D F)$ of $25-50$ is needed so the mixture has $B O D_{\text {bottle }} \leq 6-7 \mathrm{mg} / \mathrm{L}$.

A longer incubation time of 20 to 30 days is used to measure the ultimate $B O D$. The ultimate $B O D$ is proportional to the quantity of biodegradable organic compounds that were present at the start of the incubation period. The 5-day BOD is approximately two-thirds of the ultimate BOD for municipal wastewater. The BOD test is problematic in many ways, aside from taking 5-days to get a result. One
problem, because it is a bioassay, is toxicity, especially with some industrial wastewaters. COD can be used as a surrogate for biodegradable organics in wastewater even though it will measure some compounds that are not biodegradable.

## Example 7.2 Measuring BOD

Four 300 mL BOD bottles (see Figure 1.2) are used to measure the 5-day BOD of a municipal wastewater. The test conditions are given in Table 7.1. Three of the four dilutions (bottles) give valid test results. These are averaged to estimate the 5day BOD of $297 \mathrm{mg} / \mathrm{L}$, which is rounded to $300 \mathrm{mg} / \mathrm{L}$.

Table 7.1 5-day BOD test data

| Bottle <br> ID No. | Volume of <br> wastewater <br> $V(\mathrm{~mL})$ | Dilution <br> Factor <br> $D F=300 / V$ | Initial DO <br> $(\mathrm{mg} / \mathrm{L})$ | Final DO <br> $(\mathbf{d a y ~ 5 )}$ <br> $(\mathrm{mg} / \mathrm{L})$ | DO <br> depletion <br> $\Delta D O(\mathrm{mg} / \mathrm{L})$ | 5-day BOD <br> $=D F \cdot \Delta D O$ <br> $(\mathrm{mg} / \mathrm{L})$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 8 | 2 | 150 | 9.1 | 7.3 | 1.8 | 270 |
| 15 | 4 | 75 | 9.1 | 5.1 | 4 | 300 |
| 18 | 6 | 50 | 8.9 | 2.5 | 6.4 | 320 |
| 21 | 10 | 30 | 9 | $1.8 \leq 2.0$ | invalid | invalid |



Figure 7.2 a rack of bottles used for measuring the Biochemical Oxygen Demand (BOD)
7.2.4 Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) is another "lumped" or aggregate measure of organics. BOD measures oxidation by bacteria under aerobic conditions. This is the mechanism that robs streams of oxygen when they are polluted with organic wastes. BOD is what we want to know. The COD is an estimate of the ultimate BOD. COD is always larger than the ultimate BOD, which is always larger than the $\mathrm{BOD}_{5}$.

The COD test measures all organic compounds that can be oxidized to carbon dioxide with a strong chemical oxidizing agent (dichromate) under acidic conditions. This includes all carbohydrates, fats and proteins and most synthetic organic compounds. It can be measured on the whole wastewater or on the 'soluble' (filterable) fraction of a wastewater.

The COD test has two advantages. It can be completed in a few hours, compared to 5 days for the $\mathrm{BOD}_{5}$ test. It can be measured on wastewaters that are toxic to the bacteria on which the BOD test depends. This makes it useful for certain kinds of industrial wastewaters.

## Example 7.3 Measures Of Biodegradable Organics In Wastewater

The influent to a biological wastewater treatment process (e.g. an activated sludge process) contains $250 \mathrm{mg} / \mathrm{L}$ ultimate BOD and $300 \mathrm{mg} / \mathrm{L}$ COD (total oxidizable organics). The treatment removes $245 \mathrm{mg} / \mathrm{L}$ ultimate BOD so the effluent contains $5 \mathrm{mg} / \mathrm{L}$ ultimate BOD. The treatment will also remove $245 \mathrm{mg} / \mathrm{L} \mathrm{COD}$ (the same compounds that make up the ultimate BOD) and the effluent COD is $55 \mathrm{mg} / \mathrm{L}$. The non-biodegradable COD in the influent passes through to the effluent untouched by microbial action.

### 7.3 Units

Material quantities, flow rates, and concentrations are expressed in a variety of units. It is most convenient to work entirely in SI units (liters, kilograms, and meters). Gallons, pounds, and feet are still used widely in the U.S., as they were once in the UK and some other countries. Converting units is a nuisance, but many engineers sooner or later will be retrofitting an old design that used these units. Therefore, some knowledge of both systems of units is a useful complement to one's skill set.

Tables 7.2 and 7.3 give the most common units used in material balances. Volumetric flow rate is measured as liters per hour, cubic meters per second, gallons per hour, and so on. Temperature and pressure, within ordinary limits, have a negligible effect on the volume of liquids.

Air and other gases expand and contract with changes in temperature and pressure and volume must be reported either at standard conditions or at the actual temperature and pressure of the gas.

Table 7.2 Units commonly used to measure composition and flow rate

| Quantity | Units | Comments \& Conversion Factors |
| :---: | :---: | :---: |
| Density | $\begin{aligned} & \mathrm{g} / \mathrm{L}, \mathrm{~kg} / \mathrm{m}^{3} \\ & \mathrm{lb} / \mathrm{ft}^{3}, \mathrm{lb} / \mathrm{gal} \end{aligned}$ | $\begin{aligned} & 1 \mathrm{~g} / \mathrm{L}=1 \mathrm{~kg} / \mathrm{m}^{3} \\ & 1 \mathrm{lb}=453.6 \mathrm{~g} ; 1 \mathrm{~kg} / \mathrm{m}^{3}=0.06243 \mathrm{lb} / \mathrm{ft}^{3} \end{aligned}$ |
| Volume | $\begin{aligned} & \mathrm{cm}^{3}, \text { liter, } \mathrm{m}^{3} \\ & \mathrm{ft}^{3}, \mathrm{gal}(\mathrm{US}) \end{aligned}$ | $\begin{aligned} & 1 \mathrm{~m}^{3}=1000 \mathrm{~L} \\ & 1 \mathrm{~m}^{3}=35.31 \mathrm{ft}^{3} ; 1 \mathrm{~L}=0.2642 \mathrm{gal}(\mathrm{US})=0.2200 \mathrm{gal}(\mathrm{UK} \end{aligned}$ |
| Volume Flow Rate | $\begin{aligned} & \mathrm{m}^{3 / \mathrm{s}}, \mathrm{~L} / \mathrm{s} \\ & \mathrm{ft}^{3} / \mathrm{s}, \mathrm{gal} / \mathrm{h}, \mathrm{gal} / \text { day }, \mathrm{mgd} \\ & \mathrm{acfm}, \mathrm{scfm} \end{aligned}$ | $1 \mathrm{~m}^{3} / \mathrm{s}=35.31 \mathrm{ft}^{3} / \mathrm{s}$ <br> $1 \mathrm{~m}^{3} / \mathrm{s}=35.31 \mathrm{ft}^{3} / \mathrm{s} ; \mathrm{mgd}=$ million $\mathrm{gal} /$ day <br> $1 \mathrm{~m}^{3} / \mathrm{s}=15,850 \mathrm{gal} / \mathrm{min}$ (US) $=13,200 \mathrm{gal} / \mathrm{min}$ (UK) actual $\mathrm{ft}^{3} / \mathrm{min}$, standard $\mathrm{ft}^{3} / \mathrm{min}$; used in US for air flows $1 \mathrm{~m}^{3} / \mathrm{s}=2119 \mathrm{ft}^{3} / \mathrm{min}$ |
| Mass | $\mu \mathrm{g}, \mathrm{mg}, \mathrm{g}, \mathrm{kg}, \mathrm{gm}$-mole, Tonne | $1 \mathrm{~kg}=2.205 \mathrm{lb} ; 453.6 \mathrm{~g}=1 \mathrm{lb} ; 1$ Tonne $(\mathrm{T})=1000 \mathrm{~kg}$ |
| Mass Flow Rate | lb , lb-mol, ton $\mathrm{g} / \mathrm{min}, \mathrm{kg} / \mathrm{h}, \mathrm{g}-\mathrm{mol} / \mathrm{h}$ $\mathrm{lb} / \mathrm{h}, \mathrm{lb} /$ day, lb-mol/h | $1 \mathrm{lb}=453.6 \mathrm{~g}, 1 \mathrm{ton}=2000 \mathrm{lb}$ |
| Concentration | ppm, mg/kg | parts per million by weight |
|  | ppb, $\mu \mathrm{g} / \mathrm{kg}$ | parts per billion by weight |
|  | ppmv | parts per million by volume; used in gaseous mixtures |
|  | $\mu \mathrm{g} / \mathrm{L}, \mathrm{mg} / \mathrm{L}$ | $1 \mathrm{mg} / \mathrm{L}=1000 \mu \mathrm{~g} / \mathrm{L}$ for liquids; may be used for gases if volume is referenced for temperature and pressure. |
|  | $\mu \mathrm{g} / \mathrm{m}^{3}, \mathrm{mg} / \mathrm{m}^{3}$ | used for particulate concentrations in gases |
|  | weight percent | used for solid and liquid mixtures |
|  | volume percent | used for gaseous mixtures |
|  | mole fraction | mole fraction = volumetric fraction in gaseous mixtures |

Table 7.3 Some basic units and conversion factors. (USCS = U.S. customary units)

| Quantity | SI Units | SI Symbol | Conversion Factor | USCS Units |
| :--- | :--- | :---: | :---: | :---: |
| Length | meter | m | 3.281 | ft |
| Mass | kilogram | kg | 2.205 | lb |
| Flow Rate | cubic meters $\mathrm{per} \sec$ | $\mathrm{m}^{3} / \mathrm{s}$ | 35.31 | $\mathrm{ft}^{3} / \mathrm{s}$ |
| Area | square meter | $\mathrm{m}^{2}$ | 10.76 | $\mathrm{ft}^{2}$ |
| Volume | cubic meter | $\mathrm{m}^{3}$ | 35.31 | $\mathrm{ft}^{3}$ |
| Velocity | meter $/ \mathrm{sec}$ | $\mathrm{m} / \mathrm{s}$ | 2.237 | $\mathrm{mi} / \mathrm{h}$ |
| Density | kilogram $/$ meter $^{3}$ | $\mathrm{~kg} / \mathrm{m}^{3}$ | $\mathrm{lb} / \mathrm{ft}^{3}$ |  |

Material flows are expressed in terms of mass per time, such as kilograms per hour ( $\mathrm{kg} / \mathrm{h}$ ), kg-moles per hour ( $\mathrm{kg}-\mathrm{mol} / \mathrm{h}$ ), and lb/day. Mass flow is computed from the volumetric flow, density of the material, and the concentration of the pollutant in the material.

A mixture is described by giving the concentration of each species in the mixture. Concentration can be expressed as mass per unit mass, mass per unit volume, or volume per unit volume. In solids it is common to report concentration as mass per unit mass, for example mg of pollutant per kg of dry solid material. Note that $1 \mathrm{mg} / \mathrm{kg}$ is one part per million ( ppm ) on a dry mass basis. In solids and liquids, ppm is always a mass ratio. In a gas, ppm indicates one part in a million parts based on volume, and it should be identified by $\mathrm{ppm}_{\mathrm{v}}$ instead of simply as ppm .

### 7.4 Liquids, Sludge and Solids

Concentrations in liquids are given as mass per volume concentrations, such as grams per liter ( $\mathrm{g} / \mathrm{L}$ ), milligrams per liter ( $\mathrm{mg} / \mathrm{L}$ ), and micrograms per cubic meter $\left(\mu \mathrm{g} / \mathrm{m}^{3}\right)$. They may also be expressed as mass ratios, such as parts per million ( ppm ) or parts per billion (ppb).

When the specific gravity of the liquid is $1.000, \mathrm{mg} / \mathrm{L}$ and ppm are equivalent. One liter of solution weighs $1 \mathrm{~kg}=1,000,000 \mathrm{mg}$ and 1 mg pollutant in $1,000,000 \mathrm{mg}$ of solution is the same as 1 mg pollutant in 1 liter of solution. Interchanging $\mathrm{mg} / \mathrm{L}$ and ppm is acceptable for municipal sewage (which is $99.99 \%$ water), and for many industrial wastewaters, and dilute slurries of low-density solids. It should not be used for highly saline wastewater, sludge, soil, or sediments.

Concentrations of pollutants in dense slurries, sludge, sediments, soil, and other solids are given as mass ratios. It is important to make clear whether the mass of bulk material is on a dry or wet basis. A concentration of $1 \mathrm{mg} / \mathrm{kg}$ means 1 milligram of pollutant in 1 kilogram of dry material; $1 \mu \mathrm{~g} / \mathrm{kg}$ means 1 microgram of pollutant in 1 kilogram of dry material. Also, a concentration of $1 \mathrm{mg} / \mathrm{kg}$ means 1 part per million and $1 \mu \mathrm{~g} / \mathrm{kg}$ means 1 part per billion.

Concentration as a weight percent can be used for solids or liquids. To say that sludge is " $4 \%$ solids by weight" means that $4 \%$ of the total sludge mass is solids. The total sludge mass includes the water and the solids. Thus, $4 \%$ solids by weight also mean $96 \%$ water by weight. And it means 0.04 kg dry solids per kg of wet sludge.

> Example 7.4 Sludge Volume And Mass

An industry is holding $8000 \mathrm{~m}^{3}$ of dense industrial sludge that has specific gravity 1.3. Calculate the sludge mass.

## Example 7.5 Mercury In Water

A wastewater effluent of 1000 liters per hour contains an average of $6 \mu \mathrm{~g} / \mathrm{L}$ mercury $(\mathrm{Hg})$. Calculate the mass flow of mercury discharged per day ( $\mathrm{g} / \mathrm{d}$ ).

## Example 7.6 Cadmium In Sludge

How much cadmium, Cd , is added to a farm field if $20 \mathrm{~m}^{3}$ of liquid sludge that is $6 \%$ solids (by weight) is incorporated into soil? The density of the liquid sludge is $1030 \mathrm{~kg} / \mathrm{m}^{3}$. The measured concentration of cadmium in the sludge is 10 ppm , defined in terms of the dry sludge solids.

## Example 7.7 Solids In Sludge

Sludge, slurry of solids and water, is pumped from a wastewater sedimentation basin at specific gravity 1.03 , total solids concentration $6 \%$, and volumetric flow rate of $50 \mathrm{~m}^{3} / \mathrm{d}$. Calculate the mass flow rate of the sludge and the dry solids.

## Example 7.8 Sampling An Air Duct

A rectangular air duct has a total area of $3.2 \mathrm{~m}^{2}$ that has been divided into four $0.8 \mathrm{~m}^{2}$ sectors. Figure 2.4 shows the dust concentration $\left(\mathrm{mg} / \mathrm{m}^{3}\right)$ and the air velocity $(\mathrm{m} / \mathrm{s})$ data, which are at $20^{\circ} \mathrm{C}$ and 1 atm pressure. Calculate the total air flow rate and the mass emission rate for dust.

| Dust $=0.11 \mathrm{mg} / \mathrm{m}^{3}$ <br> Velocity $=4 \mathrm{~m} / \mathrm{s}$ | Dust $=0.16 \mathrm{mg} / \mathrm{m}^{3}$ <br> Velocity $=4.4 \mathrm{~m} / \mathrm{s}$ |
| :---: | :---: |
| Dust $=0.13 \mathrm{mg} / \mathrm{m}^{3}$ <br> Velocity $=4.1 \mathrm{~m} / \mathrm{s}$ | Dust $=0.15 \mathrm{mg} / \mathrm{m}^{3}$ <br> Velocity $=4.2 \mathrm{~m} / \mathrm{s}$ |

Figure 7.4 Dust and velocity data

## Example 7.9 Organic Wastewater Loading

The influent to a wastewater treatment plant has a flow of 10 million gallons per day (mgd) and a 5 -day BOD concentration of $250 \mathrm{mg} / \mathrm{L}$. What is the organic load in units of pounds of BOD per day?

- Assume the wastewater specific gravity $=1.00$
- Assume specific weight of wastewater $=8.34 \mathrm{lb} / \mathrm{gal}$


### 7.5 Gases

### 7.5.1 The Ideal Gas Law

Gases expand as temperature is increased and compress as pressure is increased, so gas volume or volumetric flow rate have no useful meaning until the corresponding gas temperature and pressure are known.

The most used "standard conditions" are those of the International Union of Pure and Applied Chemistry (IUPAC) and the National Institute of Standards and Technology (NIST). Other organizations have adopted alternative definitions of standard conditions.

Normal cubic meters per hour $\left(\mathrm{Nm}^{3} / \mathrm{h}\right)$ is the volumetric flow rate for gases at $0^{\circ} \mathrm{C}$ and $1 \mathrm{~atm}(101.325 \mathrm{kPa})$.

In the U.S. a common measure is scfm to indicate "standard cubic feet per minute' or acfm to indicate 'actual cubic feet per minute". The 'standard' refers to a reference condition known in chemistry and physics as standard temperature and pressure (STP). A similar reference condition in industrial hygiene and air pollution work is the normal condition (normal temperature and pressure, or NTP). Several widely used definitions for the reference, or "standard" conditions are given in Table 7.4.

Table 7.4 Standard conditions for various disciplines (dry air only). STP indicates standard temperature and pressure for basic science. NTP indicates normal temperature and pressure conditions used in the U.S. for industrial hygiene and air pollution.

| Discipline | Temperature | Absolute Temp. | Pressure | Organization |
| :--- | :---: | :---: | :---: | :---: |
| Chemistry/physics (STP) | $0^{\circ} \mathrm{C}$ | 273.15 K | $100.000 \mathrm{kPa}, 0.987 \mathrm{~atm}$ | IUPAC |
| Chemistry/physics (STP) | $20^{\circ} \mathrm{C}$ | 293.15 K | $101.325 \mathrm{kPa}, 1 \mathrm{~atm}$ | NIST |
| Air pollution (new sources) | $20^{\circ} \mathrm{C}$ | 293.15 K | $101.325 \mathrm{kPa}, 1 \mathrm{~atm}$ | U.S. EPA |
| Air pollution (ambient air) | $25^{\circ} \mathrm{C}$ | 298.15 K | $101.325 \mathrm{kPa}, 1 \mathrm{~atm}$ | Air pollution |
| Industrial ventilation | $21.1^{\circ} \mathrm{C}\left(70^{\circ} \mathrm{F}\right)$ | $529.67^{\circ} \mathrm{R}$ | 29.921 in Hg |  |
| Industrial hygiene | $60^{\circ} \mathrm{F}$ | $519.67^{\circ} \mathrm{R}$ | 14.696 psi | U.S. OSHA |
| ASHRAE* | $15^{\circ} \mathrm{C}\left(59.0^{\circ} \mathrm{F}\right)$ | 288.15 K | $101.325 \mathrm{kPa}, 1 \mathrm{~atm}$ |  |

* ASHRAE = American Society for Heating Refrigeration and Air Conditioning

Gas concentrations are usually measured as a volumetric ratio, typically parts per million by volume, ppmv. The ppmv concentration is independent of changes in pressure and temperature because all gases in a mixture expand or contract to the same extent. For example, if the concentration of $\mathrm{SO}_{2}$ in air is 15 ppmv , then every million volumes of air contains 15 volumes of $\mathrm{SO}_{2}$ regardless of how the gas mixture is compressed or expanded. This is one advantage of using ppmv units for air pollution work.

A mass concentration, say $\mu \mathrm{g} / \mathrm{m}^{3}$ or $\mathrm{mg} / \mathrm{m}^{3}$, is needed to make a material balance. The mass concentration is calculated using the molecular mass of the gaseous pollutant. Corrections for pressure and temperature may be required. These corrections are made using the ideal gas law:

$$
P V=n R T
$$

where $P=$ pressure, atm
$T=$ absolute temperature, K
$V=$ gas volume, L
$n=$ number of moles of gas
$R=$ universal gas constant $=0.08205 \mathrm{~L} \mathrm{~atm} /$ mole K
The value of $R$ depends on the units used for pressure, temperature, and volume, as given in Table 7.5.

Table 7.5 Values and units of the universal gas constant $R$ in the ideal gas law.

| $R$ value and units |  | Pressure | Temperature | Volume |
| :---: | :---: | :---: | :---: | :---: |
| 0.08205 L -atm/mole K |  | 1 atm | 273.15 K | $22.41 \mathrm{~L} / \mathrm{g} \mathrm{mol}$ |
| 0.08205 L -atm/mole K |  | 1 atm | 298.15 K | $22.45 \mathrm{~L} / \mathrm{g} \mathrm{mol}$ |
| $62.056 \mathrm{~L}-\mathrm{mm} \mathrm{Hg} / \mathrm{mole} \mathrm{K}$ |  | 760 mm Hg | 273.15 K | $22.41 \mathrm{~L} / \mathrm{g} \mathrm{mol}$ |
| $0.73402 \mathrm{ft}^{3}-\mathrm{atm} / \mathrm{lb} \mathrm{mol}{ }^{\circ} \mathrm{R}$ |  | 1 atm | 492.7 ${ }^{\circ} \mathrm{R}$ | $359 \mathrm{ft}^{3} / \mathrm{lb} \mathrm{mol}$ |
| $550 \mathrm{ft}^{3}-\mathrm{mm} \mathrm{Hg} / \mathrm{lb} \mathrm{mol}-{ }^{\circ} \mathrm{R}$ |  | 760 mm Hg | 492.7 ${ }^{\circ} \mathrm{R}$ | $359 \mathrm{ft}^{3} / \mathrm{lb} \mathrm{mol}$ |
| Conversions (rounded) | $\mathrm{K}={ }^{\circ} \mathrm{C}+273.15$ | ${ }^{\circ} \mathrm{R}={ }^{\circ} \mathrm{F}+459.67$ |  |  |

$V_{m}=8.3145 \times \frac{273.15}{101.325}=22.414 \frac{\mathrm{~m}^{3}}{\mathrm{~kg} \mathrm{~mol}}$ at $0^{\circ} \mathrm{C}$ and 101.325 kPa
$V_{m}=8.3145 \times \frac{273.15}{100.000}=22.711 \frac{\mathrm{~m}^{3}}{\mathrm{~kg} \mathrm{~mol}}$ at $0^{\circ} \mathrm{C}$ and 100 kPa
$V_{m}=8.3145 \times \frac{298.15}{101.325}=24.466 \frac{\mathrm{~m}^{3}}{\mathrm{~kg} \mathrm{~mol}}$ at $25^{\circ} \mathrm{C}$ and 101.325 kPa
$V_{m}=8.3145 \times \frac{298.15}{100.000}=24.790 \mathrm{mz} / \mathrm{kg} \mathrm{mol}$ at $25^{\circ} \mathrm{C}$ and 100 kPa
$V_{m}=10.7316 \times \frac{519.67}{14.696}=379.48 \frac{\mathrm{ft}^{3}}{\mathrm{lb} \mathrm{mol}}$ at $60^{\circ} \mathrm{F}$ and $14.696 \mathrm{psi}\left(0.8366 \frac{\mathrm{ft}^{3}}{\text { gram mole }}\right)$
$V_{m}=10.7316 \times \frac{519.67}{14.730}=378.61 \frac{\mathrm{ft}^{3}}{l b \mathrm{~mol}}$ at $60^{\circ} \mathrm{F}$ and 14.73 psi

## Example 7.10 Mass of a Gas

Calculate the mass of the gas that occupies a volume of 2000 L at $20^{\circ} \mathrm{C}$ and 1.2 atm and has molar mass $=16 \mathrm{~g} /$ mole. For these units the universal gas constant is $0.08205 \mathrm{~L} \mathrm{~atm} /$ mole K. Absolute temperature: $=20^{\circ} \mathrm{C}+273=293 \mathrm{~K}$.

### 7.5.2 Pollutant Concentrations in Gases

Pollutant concentrations in gases can be given in terms of volume (ppmv) or mass $\left(\mathrm{mg} / \mathrm{m}^{3}\right)$. Conversion from one form to the other is accomplished using the molar mass $(M M)$ of the pollutant and the ideal gas law. One g-mole of an ideal gas occupies a volume $0.02241 \mathrm{~m}^{3}(22.41 \mathrm{~L})$ at standard temperature and pressure $\left(0^{\circ} \mathrm{C}=\right.$ 273 K and 1 atm ). One lb-mole occupies a volume of $359 \mathrm{ft}^{3}$ at STP. Also, $1 \mathrm{~m}^{3}$ of an ideal gas contains $1 / 0.02241 \mathrm{~m}^{3}=44.623 \mathrm{~g}$-moles of the gas.
The mass ( mg ) of a gas occupying $1 \mathrm{~m}^{3}$ is

$$
\frac{\text { mass of gas }(\mathrm{mg})}{\text { volume of gas }\left(\mathrm{m}^{3}\right)}=\frac{M M\left(\frac{g}{\mathrm{~mol}}\right)}{0.0241\left(\frac{\mathrm{~m}^{3}}{\mathrm{~mole}}\right)} \times \frac{1000 \mathrm{mg}}{1 \mathrm{~g}}=\frac{M M(1000)}{0.02241}
$$

where $M M$ is the molar mass of the gas ( $\mathrm{g} / \mathrm{mole}$ ).
If a gas mixture contains a pollutant at a concentration of 1 ppmv , or $1 \mathrm{~m}^{3}$ of pollutant in $1,000,000 \mathrm{~m}^{3}$ of mixture, the mass concentration will be given by:

$$
\begin{aligned}
& \frac{m g \text { pollutant }}{m^{3} \text { mixture }}=\left(\frac{m^{3} \text { pollutant }}{10^{6} m^{3} \text { mixture }}\right)\left(\frac{M M\left(\frac{g}{m o l}\right)}{0.0241\left(\frac{m^{3}}{m o l e}\right)}\right)\left(\frac{1000 m g}{1 g}\right) \\
& \frac{m g \text { pollutant }}{m^{3} \text { mixture }}=p p m_{V}\left(\frac{M M\left(\frac{g}{m o l}\right)}{0.0241\left(\frac{m^{3}}{m o l e}\right)}\right)\left(\frac{1}{10^{6}}\right)=p p m_{V}\left(\frac{M M}{0.0241}\right)
\end{aligned}
$$

A simple adjustment is needed when the gas is at non-standard temperature and pressure. The mass of pollutant will remain constant while the volume of the gas in which it is contained expands or contracts. From the ideal gas law, the gas volumes at STP and at actual $T$ and $P$ are related by:

$$
\frac{(1 \mathrm{~atm})\left(V_{S T P}\right)}{273}=\frac{P\left(V_{T P}\right)}{T} \quad \text { or } \quad \frac{V_{S T P}}{V_{T P}}=\left(\frac{273}{T}\right)\left(\frac{P}{1 \mathrm{~atm}}\right)
$$

The mass concentration at actual $T$ and $P$ is

$$
\left(\frac{m g}{m^{3}}\right)_{T P}=\left(\frac{m g}{m^{3}}\right)_{S T P}\left(\frac{273}{T}\right)\left(\frac{P}{1 a t m}\right)
$$

where temperature is Kelvins $\left(K={ }^{\circ} C+273\right)$ and pressure is atmospheres (atm).

Pollution regulations in the United States typically reference their pollutant limits to an ambient temperature of 20 to $25^{\circ} \mathrm{C}$ as noted in Table 7.4.

## Example 7.11 Converting from Volume Concentration to Mass Concentration

The concentration of a gaseous pollutant in air is 50 ppmv . The molecular mass of the pollutant is $16 \mathrm{~g} / \mathrm{mol}$. Find the concentration as $\mathrm{mg} / \mathrm{m}^{3}$ at standard conditions.

## Example 7.12 Mass Concentration in Gases

A gaseous emission has an $\mathrm{SO}_{2}$ concentration of 25 ppmv . The gas temperature and pressure are $26^{\circ} \mathrm{C}$ and 1.1 atm . The molar mass of $\mathrm{SO}_{2}$ is $64 \mathrm{~g} / \mathrm{mole}$.

## Example 7.13 Mass Flow Of Gases

A ventilation airflow of $60,000 \mathrm{~m}^{3} / \mathrm{h}$ (at STP) from a printing company contains 1,200 ppmv toluene.

### 7.5.3 Dalton's Law of Partial Pressure

Dalton's law of partial pressure states that at constant temperature the total pressure exerted by a mixture of gases in a definite volume is equal to the sum of the individual pressures each gas would exert if it occupied the same total volume. In other words, the total pressure of a gas mixture is equal to the sum of the partial pressures of the individual components of the mixture. For a mixture of gases A, B and C , this is

$$
P_{T}=P_{A}+P_{B}+P_{C}
$$

## Example 7.14 Mixture of Four Ideal Gases

The contents of four rigid flasks of one-liter volume are to be mixed together to prepare a calibration gas mixture. The flasks contain sulfur dioxide $\left(\mathrm{SO}_{2}\right)$ at 75 mm Hg pressure, nitrogen $\left(\mathrm{N}_{2}\right)$ at 120 mm Hg , methane $\left(\mathrm{CH}_{4}\right)$ at 45 mm Hg , and carbon monoxide (CO) at 60 mm Hg . What will be the final pressure after these four flasks are combined in a one-liter flask?

$$
P_{\text {Total }}=75 \mathrm{mmHg}+120 \mathrm{mmHg}+45 \mathrm{mmHg}+60 \mathrm{mmHg}=300 \mathrm{mmHg}
$$

## Example 7.15 Apparent Molecular Mass of Dry Air

A gas that is composed of a single species has a molar mass, but a mixture of gases, such as air, does not because there is no thing as an "air molecule." Nevertheless, if one imagines that air does consist of "air molecules", a standard mixture of air can be defined and an apparent molar mass can be calculated.

The molar mass of this mixture will be the weighted average of the molar masses of each of the individual component. Each component will exert its molecular mass $\left(M_{i}\right)$ weighted by its volume fraction $\left(V_{F i}\right)$. The volume fraction is the decimal equivalent of the volume percentage. For example, air is $78.084 \%$ nitrogen by volume and the volume fraction of nitrogen is 0.78084 . The standard composition of dry air and the calculations are given in Table 7.6

Table 7.6 Composition of dry air and the calculation of the apparent molecular mass

| Component | Symbol | $\begin{gathered} \text { Molecular } \\ \text { mass } \\ \left(M_{i}\right) \\ \hline \end{gathered}$ | Concentration Percent (\%) | Volume fraction $\left(V_{\mathrm{i}} F_{\mathrm{i}}\right)$ | Contribution $\left(M_{1} V_{\mathrm{i}} F_{\mathrm{i}}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Nitrogen | $\mathrm{N}_{2}$ | 28.01 | 78.084 | 0.78084 | 21.871328 |
| Oxygen | $\mathrm{O}_{2}$ | 32.00 | 20.9476 | 0.209476 | 6.703232 |
| Argon | Ar | 39.948 | 0.934 | 0.00934 | 0.373114 |
| Carbon dioxide | $\mathrm{CO}_{2}$ | 44.00 | 0.0314 | 0.000314 | 0.013816 |
| Neon | Ne | 20.183 | 0.001818 | 0.00001818 | 0.000367 |
| Helium | He | 4.0026 | 0.000524 | 0.00000524 | 0.000021 |
| Methane | $\mathrm{CH}_{4}$ | 16.04 | 0.0002 | 0.000002 | 0.000032 |
| Sulfur dioxide | $\mathrm{SO}_{2}$ | 64.06 | 0.0001 | 0.000001 | 0.000064 |
| Hydrogen | $\mathrm{H}_{2}$ | 2.0159 | 0.00005 | 0.0000005 | 0.000001 |
| Krypton | Kr | 83.8 | 0.0000667 | 0.000000667 | 0.000056 |
| Xenon | Xe | 131.3 | 0.0000667 | 0.000000667 | 0.000088 |
| Ozone | $\mathrm{O}_{3}$ | 48.00 | $\underline{0.0000667}$ | 0.000000667 | $\underline{0.000032}$ |
|  |  |  | 99.9999 |  | $\sum \underline{M}_{i} \underline{V}_{i} F_{i}=28.9622$ |

7.5.4 Adjusting Pollutant Concentrations to Reference Conditions

Air pollutant concentrations sometimes must be adjusted or 'corrected' to concentrations at specified reference conditions of moisture content, oxygen content or carbon dioxide content. For example, a regulation might limit the concentration in a dry combustion exhaust gas to $55 \mathrm{ppmv} N O x$ (at a specified reference temperature and pressure) corrected to 3 volume percent $\mathrm{O}_{2}$ in the dry gas. Another regulation might limit the concentration of total particulate matter to $200 \mathrm{mg} / \mathrm{m}^{3}$ of an emitted gas (at a specified reference temperature and pressure) corrected to a dry basis and further corrected to 12 volume percent $\mathrm{CO}_{2}$ in the dry gas. The adjustments are explained by example.

Environmental agencies in the U.S. often use the terms $s c f d$ (or $d s c f$ ) to denote a 'standard' cubic foot of dry gas. Likewise, scmd (or dscm) denotes a 'standard' cubic meter of gas. Since there is no universally accepted set of 'standard' temperature and pressure, such usage can be confusing. It is recommended that the reference temperature and pressure always be clearly specified when stating gas volumes or gas flow rates.

## Example 7.16 Adjusting Gas Composition to A Dry Basis

A gaseous emission has a pollutant concentration of $C_{\text {wet basis }}=40 \mathrm{ppmv}$ and 10 volume percent of water vapor. The 40 ppmv should be designated as the "wet basis" pollutant concentration. The adjustment of the measured "wet basis" concentration to a "dry basis" concentration is done using

$$
C_{d r y ~ b a s i s}=\frac{C_{w e t ~ b a s i s}}{1-W}
$$

where: $C=$ Concentration of the air pollutant in the emitted gas
$W=$ fraction, by volume, of water vapor in the emitted gas

$$
C_{d r y \text { basis }}=\frac{C_{w e t ~ b a s i s ~}}{1-W}=\frac{40}{1-0.1}=44.4 \mathrm{ppmv}
$$

## Example 7.17 Adjusting Gas Composition to a Reference Oxygen Content

A measured $\mathrm{NO}_{\mathrm{x}}$ concentration of 45 ppmv in a dry gas having 5 volume \% $\mathrm{O}_{2}$. This is adjusted to give a measured pollutant concentration in a dry emitted gas with a measured $\mathrm{O}_{2}$ content to an equivalent pollutant concentration in a dry emitted gas with a specified reference amount of $\mathrm{O}_{2}$ using

$$
C_{R}=C_{M}\left(\frac{20.9-\left(\% O_{2}\right)_{R}}{20.9-\left(\% O_{2}\right)_{M}}\right)
$$

where: $C_{R}=$ corrected concentration of a dry gas with a specified reference volume $\% \mathrm{O}_{2}$ $C_{M}=$ measured concentration in a dry gas having a measured volume $\% \mathrm{O}_{2}$ $\left(\%_{2}\right)_{R}=$ percentage of oxygen in the reference volume $\left(\% O_{2}\right)_{M}=$ percentage of oxygen in the measured volume

The $\mathrm{NO}_{\mathrm{x}}$ concentration, when corrected to a dry gas having a specified reference $\mathrm{O}_{2}$ content of 3 volume $\%$ is:

$$
C_{R}=C_{M}\left(\frac{20.9-\left(\% O_{2}\right)_{R}}{20.9-\left(\% O_{2}\right)_{M}}\right)=45\left(\frac{20.9-3.0}{20.9-5.0}\right)=50.7 \mathrm{ppmv}^{2} N O_{x}
$$

Note: The measured gas concentration $C_{m}$ must first be corrected to a dry basis before using the above equation.

## Example 7.18 Adjusting Gas Composition to a Reference Carbon Dioxide Content

A dry gas has a measured particulate concentration is $200 \mathrm{mg} / \mathrm{m}^{3}$ and a measured 8 volume $\% \mathrm{CO}_{2}$. This can be corrected to an equivalent pollutant concentration in an emitted gas that has a specified reference amount of 12 volume \% of $\mathrm{CO}_{2}$.

### 7.6 Conclusion

Pollutants have many physical and chemical forms. They may be carried by water or some other liquid, or by air or some other gas, or they may be part of a solid material, such as soil. They may be dissolved or particulate.

Specific chemicals, such as copper, chlorine, or benzene, are measured as copper, chlorine, or benzene. In wastewater treatment, pollutants with similar properties are lumped together because it is too difficult to measure individual species or simply because it is not necessary. Suspended solids, volatile solids, dissolved solids, biochemical oxygen demand, and chemical oxygen demand are 'lumped' measurements.

Likewise, environmental quality standards may be written for specific chemicals, which are the case for toxic air and water pollutants, or for lumped parameters in most municipal wastewater effluents.

This variety of pollutant forms and measurements generates the need to use a variety of units, such as $\mathrm{mg} / \mathrm{L}$ in water, $\mathrm{mg} / \mathrm{kg}$ in solids, and volume percent or ppmv in air and gases.

The difficulty in working with unfamiliar units is not making the arithmetic conversions between systems. It is losing one's sense of the magnitude of quantities. Working in treatment plants where flows are measured in gallons and million gallons, and where pipes are measured in inches, gives the experienced engineer an instinctive sense of the correct size. Working in cubic meters and centimeters creates a questioning attitude of "How big is that?" or "Does that seem about the right size." We hope students who use this book are not too much troubled by that feeling, when the examples are in unfamiliar units.

