## UNITS OF CONCENTRATION

There are a number of different ways of expressing solute concentration that are commonly used. Some of these are listed below.

Molarity, $\mathbf{M}=$ moles solute/liter of solution
Normality, $\mathbf{N}=$ equivalents of solute/liter of solution

Weight \%, Wt \% = mass ratio x $100 \%=$ mass of solute/mass of solution $\times 100 \%$
Parts per million, $\mathbf{p p m}=$ mass ratio $\times 10^{6}=$ mass of solute $/$ mass of solution $\times 10^{6}$
Mass per volume, $\mathbf{m g} / \mathbf{L}=$ mass of solute/liter of solution
molality, $\boldsymbol{m}=$ moles of solute $/$ mass of solvent $(\mathrm{kg})$
mole fraction, $\chi=$ moles of solute/total moles of solution

Concentrations expressed as N are less familiar to most students at this stage.

## Parts per million:

Parts per million concentrations are essentially mass ratios (solute to solution) x a million $\left(10^{6}\right)$. In this sense, they are similar to wt $\%$, which could be thought of as parts per hundred (although nobody uses this term). Since $10^{6}$ milligrams $=1 \mathrm{~kg}, 1 \mathrm{mg} / \mathrm{kg}$ is equivalent to 1 ppm . Similarly, $1 \mu \mathrm{~g} / \mathrm{g}$ and $1 \mathrm{ng} / \mathrm{mg}$ are also equivalent to 1 ppm .

Given that the density of dilute aqueous solutions is $\sim 1.00 \mathrm{~kg} / \mathrm{L}, 1 \mathrm{mg} / \mathrm{L}$ of solute in freshwater $\approx 1 \mathrm{ppm}$. This is true for most freshwater and other dilute aqueous solutions, but not the case for seawater and concentrated wastewater solutions, where the density of the solution is greater than $1.00 \mathrm{~kg} / \mathrm{L}$.

Other variations on this theme include: ppt - parts per thousand (used for common ions in sea water) ppb - parts per billion (used for trace heavy metals and organics) pptr - parts per trillion (used for ultratrace metals and organics)

The following table summarizes common mass ratios for solutions and solids.

| Unit | In General |  | Dilute Aqueous Solutions |  |
| :---: | :---: | :---: | :---: | :---: |
| ppm | $\mathrm{mg} / \mathrm{kg}$ | $\mu \mathrm{g} / \mathrm{g}$ | $\mathrm{mg} / \mathrm{L}$ | $\mu \mathrm{g} / \mathrm{mL}$ |
| ppb | $\mu \mathrm{g} / \mathrm{kg}$ | $\mathrm{ng} / \mathrm{g}$ | $\mu \mathrm{g} / \mathrm{L}$ | $\mathrm{ng} / \mathrm{mL}$ |
| pptr | $\mathrm{ng} / \mathrm{kg}$ | $\mathrm{pg} / \mathrm{g}$ | $\mathrm{ng} / \mathrm{L}$ | $\mathrm{pg} / \mathrm{mL}$ |

To convert concentrations in $\mathrm{mg} / \mathrm{L}$ ( or ppm in dilute aqueous solution) to molarity, divide by the molar mass of the analyte to convert mass in mg into a corresponding number of moles.

Example: What is the molarity of a $6.2 \mathrm{mg} / \mathrm{L}$ solution of $\mathbf{O}_{\mathbf{2}}(\mathrm{aq})$ in freshwater?

To convert from molarity to $\mathrm{mg} / \mathrm{L}$ (or ppm in dilute aqueous solution), multiply by the molar mass of the analyte to convert moles into corresponding number of moles.

Example: The Maximum Acceptable Concentration (MAC) of $\mathbf{P b}$ in drinking water is 10 ppb. If a sample has concentration of 55 nM , does it exceed the MAC?

In seawater, $1.00 \mathrm{mg} / \mathrm{L} \neq 1.00 \mathrm{ppm}$ since the density of seawater is $1.035 \mathrm{~kg} / \mathrm{L}$. Hence, $1.00 \mathrm{mg} / \mathrm{L}_{\text {seawater }}=1.00 \mathrm{mg} / \mathrm{L} \times 1 \mathrm{~L} / 1.035 \mathrm{~kg}=0.966 \mathrm{mg} / \mathrm{kg}$ or 0.966 ppm

Example: The concentration of $\mathrm{K}^{+}$in seawater is reported as 10.6 mM . Convert this conc to ppm.

Oceanographers often report concentrations in units of moles $/ \mathrm{kg}$.
Example: Convert $6.2 \mathrm{mg} / \mathrm{L}$ of $\mathrm{O}_{2}$ in seawater to $\mu \mathrm{mol} / \mathrm{kg}$.

Some concentrations are expressed in terms the species actually measured e.g., $\mathrm{mg} / \mathrm{L}$ of $\mathrm{NO}_{3}{ }^{-}$(mass of nitrate ions per liter)

Or in terms of a particular element in a species that was measured. e.g., $\mathrm{mg} / \mathrm{L}$ of $\mathrm{NO}_{3}{ }^{-}-\mathbf{N}$ (mass of nitrogen in the form of nitrate ions per liter)

To convert from one to the other of these, use the molar mass ratio of the element to that of the chemical species measured. In the example above use, $14 \mathrm{mg} \mathrm{N} / 62 \mathrm{mg} \mathrm{NO} \mathbf{3}^{-}$. It is important to clearly report unit values to avoid serious error in interpretation of results. Similar situations arise in reporting the concentrations of ammonia-nitrogen, phosphate-phosphorous and others.

Example: A water sample has a measured phosphate concentration of $6.8 \mu \mathrm{M}$. Express this as $\mu \mathrm{g} / \mathrm{L} \mathbf{P O}_{4}{ }^{\mathbf{3 -}}$ and $\mathrm{ppb} \mathbf{P O}_{4}{ }^{\mathbf{3}}-\mathbf{P}$.

Some aggregate parameters are reported in terms of a single surrogate species.
e.g., total hardness is usually reported as the mass of $\mathbf{C a C O}_{3}$ that would be required to provide the same number of moles of calcium ions.

Example: A groundwater sample has been determined to contain 100. ppm Ca and 80. ppm Mg by flame atomic absorption spectrophotometry. Express the total hardness as ppm $\mathrm{CaCO}_{3}$.

Example: A water sample has been found to contain 0.6 mM of $\mathbf{A s}, \mathbf{F}^{-}$and $\mathbf{N O}_{3}{ }^{-}$. The drinking water guidelines for arsenic, fluoride and nitrate-nitrogen are $10 \mathrm{ppb}, 1.5 \mathrm{ppm}$ and 10 ppm , respectively. Does this sample exceed the drinking water guidelines for arsenic, fluoride or nitrate - nitrogen?

Example: A commercial bleach solution $\mathbf{N a O C l}(\mathrm{aq})$ is reported to be $12.5 \%$ (weight). If the density is $1.05 \mathrm{~g} / \mathrm{mL}$, calculate the molar concentration.

Example: A standard solution is prepared by dissolving 225 mg of sodium thiosulfate pentahydrate in a one litre volumetric flask. After thoroughly mixing, 5.00 mL was transferred to a 250 . volumetric flask and diluted to the mark. What is the molar concentration of thiosulfate in the final solution?

Normality is a concentration unit that is still encountered in many texts and lab manuals. It has particular advantages when carrying out acid/base and redox titration calculations, however it can be confusing for the uninitiated. Normality is defined as the number of equivalents of solute per liter, where an equivalent is defined as a mole of reacting species ( $\mathbf{H}^{+}$or $e-$ ). Normality is always a multiple of Molarity.
$\mathrm{N}=\mathrm{K} \times \mathrm{M}$
where $\mathrm{K}=$ \#equivalents per mole, K is an integer constant $\geq 1$
Hence;
Equiv. Weight = M.W./K
and
\# equivalents of solute = mass of solute/equiv. weight
K for a particular species is defined by the context of the chemical reaction (acid/base vs redox) and the number of moles of $\mathbf{H}^{+}$or $e$ - exchanged per mole of reacting substance.

For acid/base rxn's: K is the number of moles of $\mathbf{H}^{+}$ions produced or neutralized per mole of acid or base supplied. Thus,

| Acid/base | $\mathbf{K}$ <br> (equiv/mol) | M.W. <br> $(\mathrm{g} / \mathrm{mol})$ | E.W. <br> $(\mathrm{g} /$ equiv) |
| :---: | :---: | :---: | :---: |
| $\mathbf{H C l}$ | 1 | 36.5 | 36.5 |
| $\mathbf{H}_{\mathbf{2}} \mathbf{S O}_{4}$ | 2 | 98.1 | 49.0 |
| $\mathbf{C a C O}_{3}$ | 2 | 100 | 50.0 |
| $\mathbf{A l}(\mathbf{O H})_{\mathbf{3}}$ | 3 | 78.0 | 26.0 |

Thus, for the reaction;

$$
\mathrm{CaCO}_{3}+2 \mathbf{H}^{+} \rightarrow \mathrm{Ca}^{2+}+\mathbf{H}_{2} \mathbf{C O}_{3}
$$

there are 2 moles of $\mathbf{H}^{+}$transferred per each mole of $\mathbf{C a C O}_{3}$ reacted, so K for $\mathbf{C a C O}_{3}$ (in this context) is equal to 2 equiv/mol and the equivalent weight of $\mathbf{C a C O}_{3}$ is equal to 50 g/equiv.

For oxidation/reduction reactions, K is the number of moles of $e$ - transferred per mole of oxidant or reductant in the balanced half-reaction.

| Balanced half reaction | $\mathbf{K}$ (equiv/mol) |
| :---: | :---: |
| $\mathbf{F e}^{\mathbf{3 +}} \rightarrow \mathbf{F e}$ | 3 |
| $\mathbf{I}_{\mathbf{2}} \rightarrow 2 \mathbf{I}^{-}$ | 2 |
| $2 \mathbf{S}_{\mathbf{2}} \mathbf{O}_{\mathbf{3}}{ }^{2-} \rightarrow \mathbf{S}_{\mathbf{4}} \mathbf{O}_{\mathbf{6}}{ }^{2-}$ | 1 |

Thus, for the reaction;

$$
\mathbf{I}_{2}+2 \mathbf{S}_{\mathbf{2}} \mathbf{O}_{3}{ }^{2-} \rightarrow 2 \mathbf{I}^{-}+\mathbf{S}_{4} \mathbf{O}_{6}{ }^{2-}
$$

there are 2 moles of electrons transferred per mole of $\mathbf{I}_{\mathbf{2}}$ reacted, so K for $\mathbf{I}_{\mathbf{2}}$ (in this context) is 2 equiv $/ \mathrm{mol}$.

## Working with Normality in titration calculations

Method 1: Use the appropriate conversion factor ( $\mathrm{K}=$ \#equiv/mol) to convert Normality to Molarity, (i.e., $0.250 \mathrm{~N}_{\mathbf{2}} \mathbf{S O}_{4}=0.125 \mathrm{M} \mathrm{H}_{\mathbf{2}} \mathbf{S O}_{4}$ ) and use the coefficients in the balanced chemical equations to solve for the number of moles of analyte in given sample volume.

Method 2: Use the Normal concentrations directly and convert your final analyte concentration from \#equiv/L to moles/L or mg/L using K or E.W., respectively. Although you will need to know the chemical form of the analyte in the final product, you do not need the balanced chemical equations.
\# of equiv. of analyte = \# equiv. titrant
This is particularly useful in volumetric determinations, where we can always write;
$\mathbf{N}_{\text {analyte }} \times \mathbf{V}_{\text {analyte }}=\mathbf{N}_{\text {titrant }} \times \mathbf{V}_{\text {titrant }}$
regardless of the complexity of the reaction chemistry involved.

## EXAMPLES

1. When 25.00 mL of $\mathbf{N a O H}$ solution was titrated with $0.572 \mathrm{~N} \mathrm{H}_{\mathbf{2}} \mathbf{S O}_{4}, 23.40 \mathrm{~mL}$ of was required to reach the end point. Find the molarity of the $\mathbf{N a O H}$.

## Method 1

Method 2
2. The Winkler titration for the determination of dissolved oxygen involves the treatment of the sample with iodide ion $\left(\mathbf{I}^{-}\right)$in the presence of manganese ion catalyst $\left(\mathbf{M n}^{2+}\right)$ as follows.

$$
\begin{aligned}
& \mathbf{O}_{\mathbf{2}}+2 \mathbf{M n}^{\mathbf{2 +}}+4 \mathbf{O H}^{-} \rightarrow 2 \mathbf{M n O}_{\mathbf{2}}(\mathrm{s})+2 \mathbf{H}_{2} \mathbf{O} \\
& \mathbf{M n O}_{\mathbf{2}}(\mathrm{s})+4 \mathbf{H}^{+}+2 \mathbf{I}^{-} \rightarrow \mathbf{M n}^{2+}+\mathbf{I}_{\mathbf{2}}+2 \mathbf{H}_{\mathbf{2}} \mathbf{O}
\end{aligned}
$$

The liberated iodine is then titrated with a standard thiosulfate solution.

$$
\mathbf{I}_{2}+2 \mathbf{S}_{2} \mathbf{O}_{3}{ }^{2-} \rightarrow 2 \mathbf{I}^{-}+\mathbf{S}_{4} \mathbf{O}_{6}{ }^{2-}
$$

A 50.00 mL sample of water was treated as above and the $\mathbf{I}_{\mathbf{2}}$ liberated was titrated with 8.11 mL of $0.01136 \mathrm{~N} \mathrm{Na}_{2} \mathbf{S}_{2} \mathbf{O}_{3}$ to reach the end point. Determine the concentration of the dissolved $\mathbf{O}_{\mathbf{2}}$ in equiv./L, moles/L and $\mathrm{mg} / \mathrm{L}$.

## More on those darn Normalities

Normality ( $N$ ) is an expression of solute concentration like Molarity (M), except that it takes into account the actual number of reacting species per mole of reagent (i.e., protons in the case of acid/base reactions or electrons in the case of redox reactions). For acids, an equivalent is defined as one mole of protons. The equivalent amount of any acid is the amount of acid that delivers one mole of $\mathbf{H}^{+}$. So for $\mathbf{H}_{2} \mathbf{S O}_{4}$, one equivalent is $1 / 2$ of one mole, since each mole of $\mathbf{H}_{2} \mathbf{S O}_{4}$ produces two moles of $\mathbf{H}^{+}$. Consequently, the equivalent weight is half of the molecular weight. Similarly, for bases an equivalent amount of a base is defined as the amount of base that neutralizes one mole of $\mathbf{H}^{+}$. For $\mathbf{C a C O}_{3}$, one equivalent is $1 / 2$ of one mole, since each mole of $\mathbf{C a C O}_{3}$ neutralizes two moles of $\mathbf{H}^{+}$. And again, the equivalent weight is $1 / 2$ the molecular weight.

Put another way, K (which is an expression of the number of equivalents supplied per mole of a substance) is equal to the number of moles of $\mathbf{H}^{+}$produced per mole of substance. Thus, $\mathrm{K}=1$ equiv/mole for $\mathbf{H C l}$ and $\mathbf{N a O H}$, but $\mathrm{K}=2$ equiv/mole for $\mathbf{H}_{2} \mathbf{S O}_{4}$ and $\mathbf{C a C O}_{3}$.

For redox rxns, an equivalent is defined as the amount of a substance that delivers one mole of electrons. So for the reaction in which

$$
\mathrm{O}_{\mathbf{2}} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}
$$

The oxidation state of each oxygen atom drops from 0 to -2 . Thus, a total of 4 equivalents have been transferred for each mole of $\mathbf{O}_{2}$ reacted and $\mathrm{K}=4$ equiv/mole.

Put another way, K (which is an expression of the number of equivalents supplied per mole of a substance) is equal to the number of moles of e- produced per mole of substance. For the reaction

$$
2 \mathbf{S}_{2} \mathbf{O}_{3}{ }^{2-} \rightarrow \mathbf{S}_{4} \mathbf{O}_{6}{ }^{2-}
$$

The oxidation state on each sulfur increases from 2 to 2.5 (on average) for a net change of $1 / 2 \operatorname{per} \mathbf{S}$ atom. Since there are two $\mathbf{S}$ atoms per $\mathbf{S}_{\mathbf{2}} \mathbf{O}_{3}{ }^{2-}$, each mole of thiosulfate is involved in the transfer of 1 equivalent of $\mathrm{e}-$ in reacting to form $\mathbf{S}_{\mathbf{4}} \mathbf{O}_{6}{ }^{2-}$. Thus $\mathrm{K}=1$.

| Conversion Chart for Concentrations of $\mathbf{O}_{\mathbf{2}}$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{FROM} \quad \mathrm{TO} \rightarrow$ | $\mathrm{mg} \mathbf{O}_{\mathbf{2}} / \mathrm{L}$ | $\operatorname{moles} \mathbf{O}_{\mathbf{2}} / \mathrm{L}$ | equiv $\mathbf{O}_{\mathbf{2}} / \mathrm{L}$ |  |
| $\mathrm{mg} \mathrm{\mathbf{O}}_{\mathbf{2}} / \mathrm{L}$ | - | $1 \mathrm{~mol} / 32,000 \mathrm{mg}$ | 1 equiv/8000 mg |  |
| moles $\mathbf{O}_{\mathbf{2}} / \mathrm{L}$ | $32,000 \mathrm{mg} / \mathrm{mol}$ | - | 4 equiv/mol |  |
| equiv $\mathbf{O}_{\mathbf{2}} / \mathrm{L}$ | $8000 \mathrm{mg} /$ equiv | $1 \mathrm{~mol} / 4$ equiv | - |  |

Construct a similar conversion table for $\mathbf{C a C O}_{3}$. Other conversion charts can be prepared that include converting to $\mathrm{mg} / \mathrm{L} \mathrm{NO}_{3}{ }^{-}-\mathbf{N}, \mathrm{mg} / \mathrm{L} \mathbf{N O}_{3}{ }^{-}$and mM .

