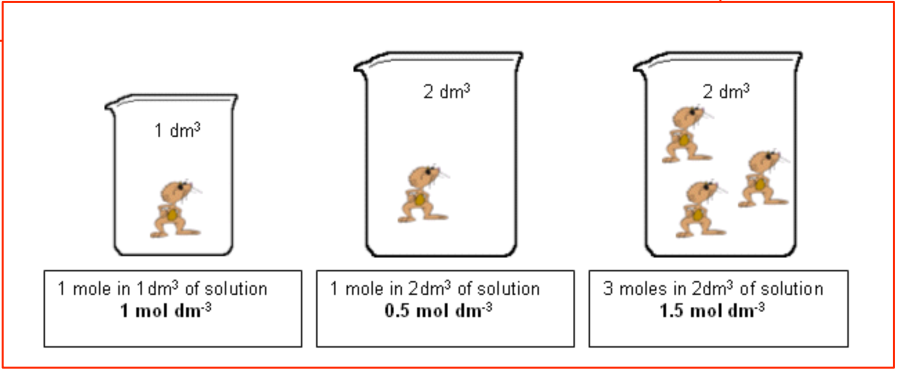
MEASURING CONCENTRATIONS

Concentrations of elements or compounds are measured in a few common ways. Only in rare cases do scientists directly measure individual atoms/compounds, for even microscopic crystals of minerals at the micrometer scale such as hydroxides and silicate clays typically contain millions or billions of atoms.

concentrations
=
relative
abundance



Mass-based concentrations

One common means of measuring concentrations is by units such as milligrams per kilogram (mg/kg) for solids and milligrams per liter (mg/L) for liquids, or sometimes in units of micrograms (µg/kg or µg/L) or nanograms (ng/kg or ng/L) for trace elements. Note that mg/L = µg/mL.

Weight percent is a common mass-based approach for expressing element concentration in cases where elements are in high concentrations

a good example being Si, which comprises approximately 28% by weight (or mass) of the continental crust or, as wt% oxide, approximately 59% of the crust –

In the case of converting Ca to CaO, the conversion is determined as the molar mass of CaO divided by the molar mass of Ca, i.e. $56.08 \div 40.08 = 1.399$.

In the case of Al_2O_3, the conversion factor is determined as the molar mass of Al_2O_3 divided by the mass of the equivalent amount of Al in the oxide, i.e. $Al_2O_3 \div (2 * Al) = 101.957 \div (2 * 26.98) = 1.889$. For Na to Na_2O, the conversion is the molar mass of Na_2O divided by the molar mass of $2 * Na = 61.98 \div (2 * 22.99) = 1.348$.

For elements that can occur in more than one oxidation state (e.g. Fe^{+2}, Fe^{+3}), values may be presented as either one of the oxidation states (i.e. either as FeO or Fe_2O_3), or as a combination of the two if the relative abundances of Fe^{+2} and Fe^{+3} are known. In many cases where iron oxidation state is not known, all iron is presented in terms of Fe_2O_3.

Molar concentrations

Quantifying concentrations on a molar basis has its roots in the work of Italian scientist Amadeo Avogrado, who in 1811 realized that equal volumes of gases at identical pressures and temperatures contain equal numbers of atoms (or molecules in the case of gases like N_2 and O_2), even though their atomic masses differed.


(1776 – 1856)

Same volume
=
Same molecules number

The term **mole** (abbreviated mol) describes the number of atoms of a given element required to form a mass equal to the atomic mass of the substance, in grams. For C, this mass is 12.011 grams. For U, this mass is 238.03 g, and so on. For all elements, the number of atoms required to form the atomic mass in grams is 6.0221×10^{23} atoms, a value known as **Avogadro's number**. 238.03 g of uranium (1 mol of U) contains 6.0221×10^{23} atoms; 4.002 g of helium (1 mol of He) contains 6.0221×10^{23} atoms.

The mole is a very useful concept in chemistry – most equations are expressed in terms of moles of reactants and products. In order to express Ni and U concentrations in terms of moles per liter (mol/L), or for trace elements like these, µmol/L, the mass concentration must be multiplied by the inverse of the molar mass (and a conversion for g to µg) as follows:

$$\text{For Ni}: \quad 98.7 \mu g/\text{L} * 1\,\text{mol}/58.693\,\text{g} * 1\,\text{g}/10^6 \mu g$$
$$= 1.68 \times 10^{-6} \text{mol}/\text{L}$$
$$\text{For U}: \quad 98.7 \mu g/\text{L} * 1\,\text{mol}/238.03\,\text{g} * 1\,\text{g}/10^6 \mu g$$
$$= 0.415 \times 10^{-6} \text{mol}/\text{L}$$

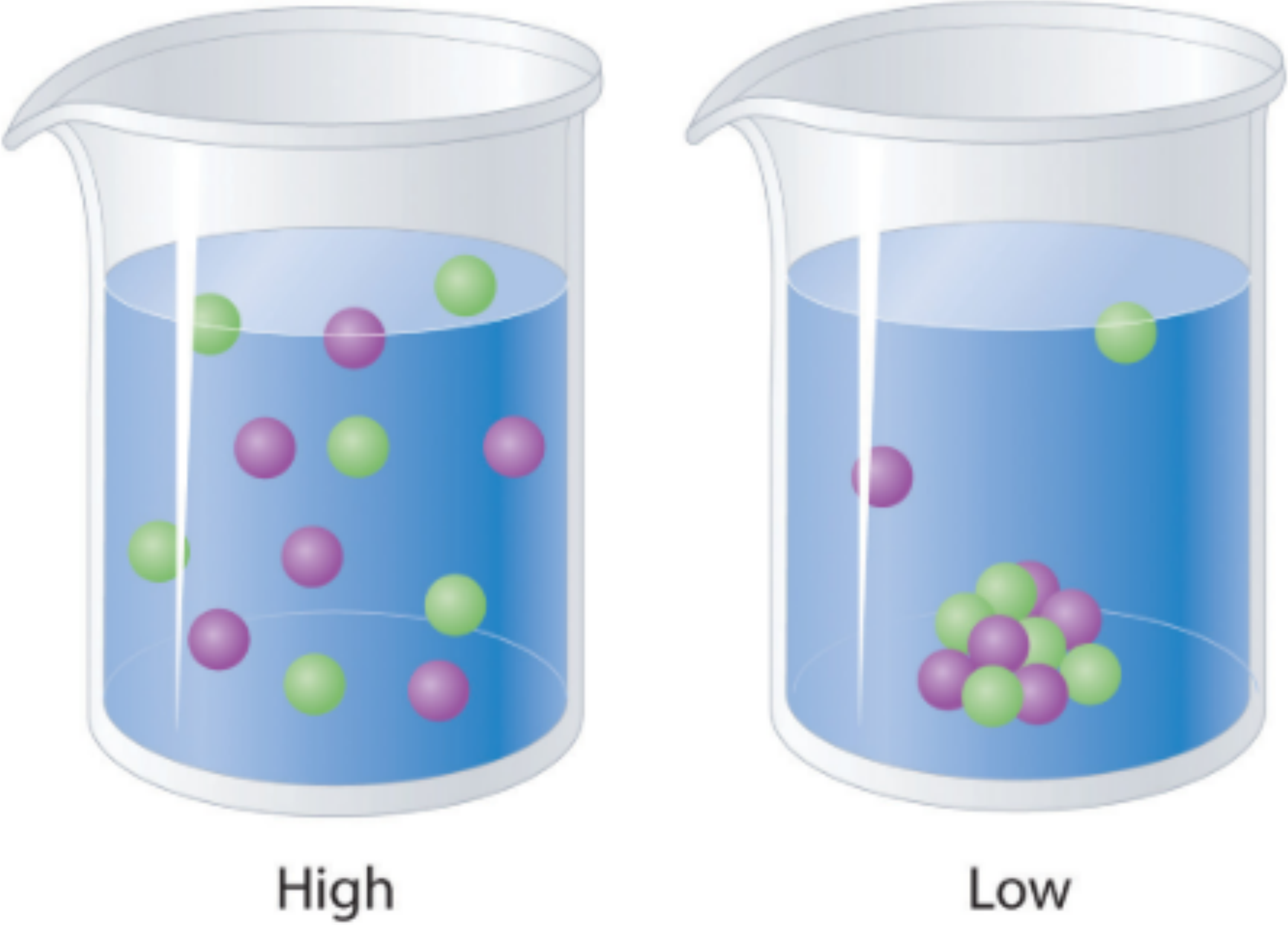
It is often helpful to express units in easy to communicate terms, so in this case mol/L would probably be converted to micromoles per liter (μmol/L), by multiplying mol/L by 10^6 μmol/mol:

$$1.68 \times 10^{-6} \text{mol/L} * 10^{6} \mu\text{mol/mol} = 1.68 \mu\text{mol/L}$$

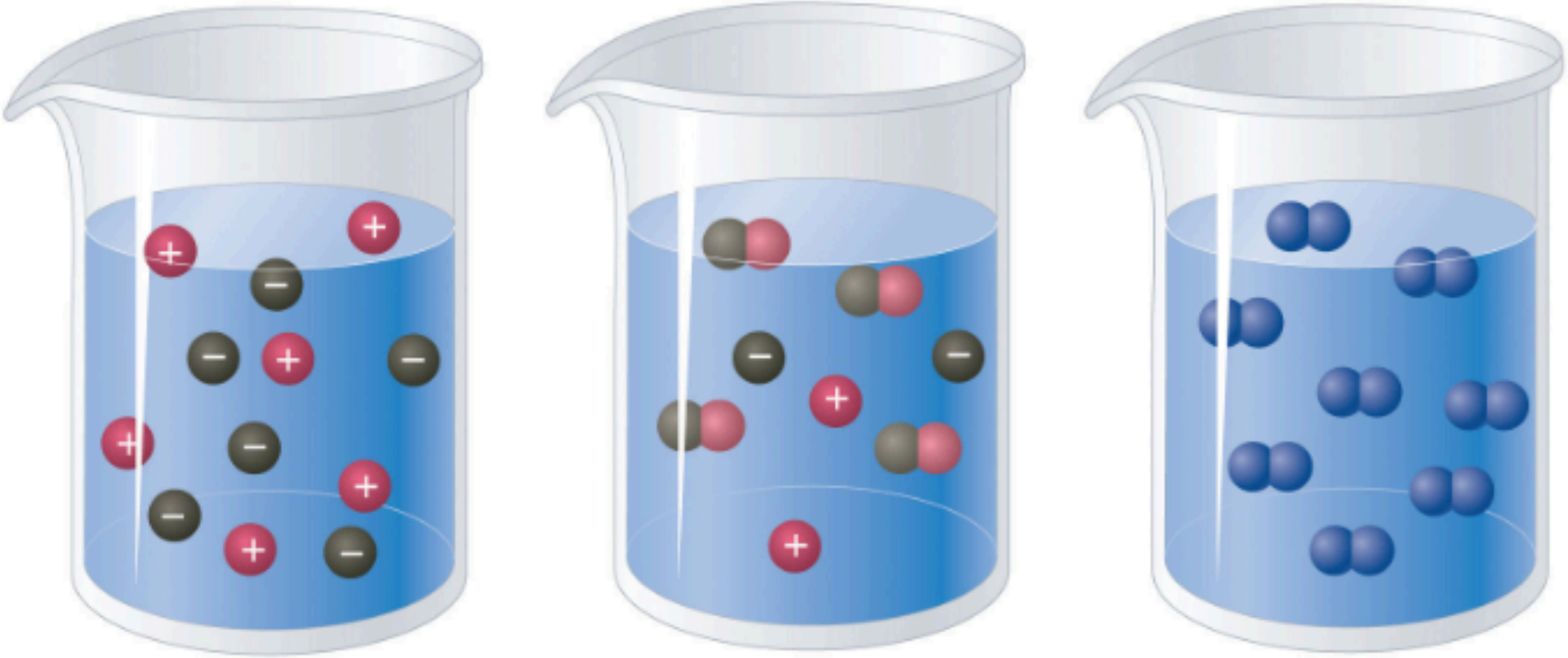
of U in the groundwater

$$0.415 \times 10^{-6} \text{mol/L} * 10^{6} \mu\text{mol/mol} = 0.415 \mu\text{mol/L}$$

of Ni in the groundwater



(a) Compound solubility



Strong Weak None

(b) Electrical conductivity

Given that 1 mol of Fe = 55.85 g:

55.85 g/mol * 1 mol/kg = 55.85 g/kg Fe

...***or*** 55.85 g/kg * 1000 mg/g = 55850 mg/kg Fe

... ***or*** 55.85 g/kg * 0.1 = 5.855% Fe (by weight)

1 mol of Al = 27 g; 27 g/mol * 1 mol/kg = 27 g/kg Al

... ***or*** 26.98 g/kg * 1000 mg/g = 26980 mg/kg Al

... ***or*** 26.98 g/kg * 0.1 = 2.698% Al (by weight)

A few other useful facts to know about units of concentrations are:

For solids:

mg/kg is also known as parts per million (ppm), where mg is a milligram (10^{-3}g)

µg/kg is also known as parts per billion (ppb), where µg is a microgram (10^{-6}g)

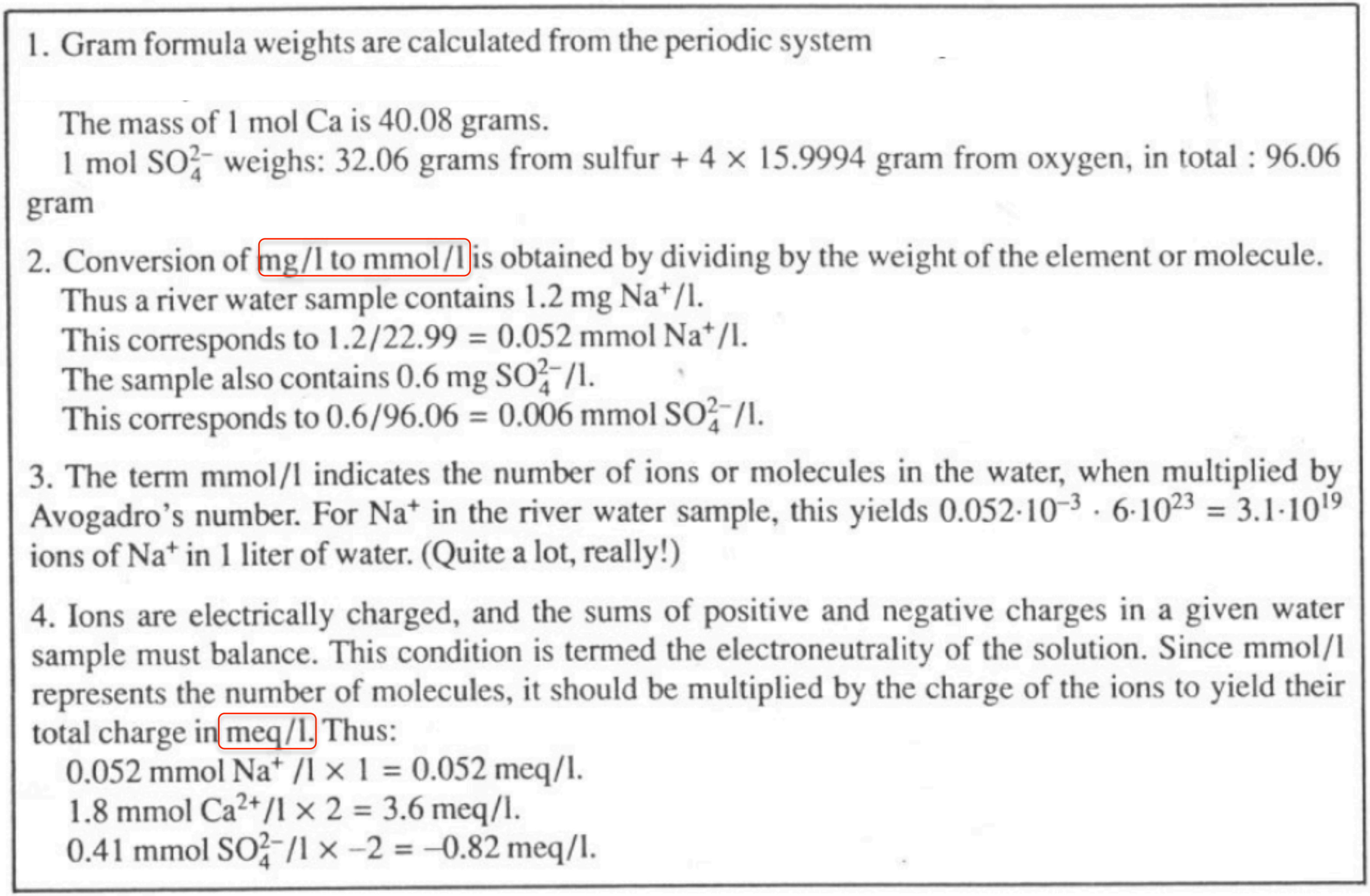
ng/kg is also known as parts per trillion (ppt), where ng is a nanogram (10^{-9}g)

For liquids:

mg/L is also known as parts per million (ppm)

µg/L is also known as parts per billion (ppb)

ng/L is also known as parts per trillion (ppt)



1. Gram formula weights are calculated from the periodic system

The mass of 1 mol Ca is 40.08 grams.

1 mol SO_4^{2-} weighs: 32.06 grams from sulfur + 4 × 15.9994 gram from oxygen, in total : 96.06 gram

2. Conversion of mg/l to mmol/l is obtained by dividing by the weight of the element or molecule.

Thus a river water sample contains 1.2 mg Na^+/l.

This corresponds to $1.2/22.99 = 0.052$ mmol Na^+/l.

The sample also contains 0.6 mg SO_4^{2-}/l.

This corresponds to $0.6/96.06 = 0.006$ mmol SO_4^{2-}/l.

3. The term mmol/l indicates the number of ions or molecules in the water, when multiplied by Avogadro's number. For Na^+ in the river water sample, this yields $0.052 \cdot 10^{-3} \cdot 6 \cdot 10^{23} = 3.1 \cdot 10^{19}$ ions of Na^+ in 1 liter of water. (Quite a lot, really!)

4. Ions are electrically charged, and the sums of positive and negative charges in a given water sample must balance. This condition is termed the electroneutrality of the solution. Since mmol/l represents the number of molecules, it should be multiplied by the charge of the ions to yield their total charge in meq/l. Thus:

0.052 mmol Na^+ /l × 1 = 0.052 meq/l.

1.8 mmol Ca^{2+}/l × 2 = 3.6 meq/l.

0.41 mmol SO_4^{2-}/l × –2 = –0.82 meq/l.

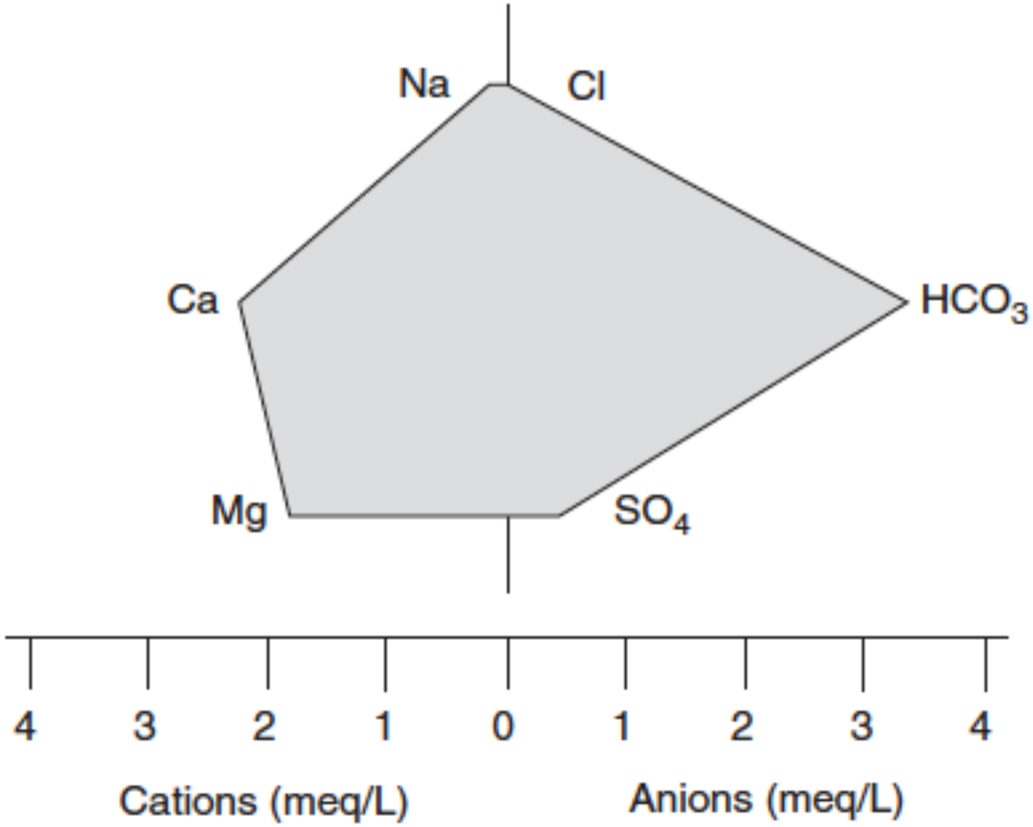
Recalculation of analysis units.

$\text{mmol/l} = \text{mg/l} \,/\, (\text{gram formula weight}).$

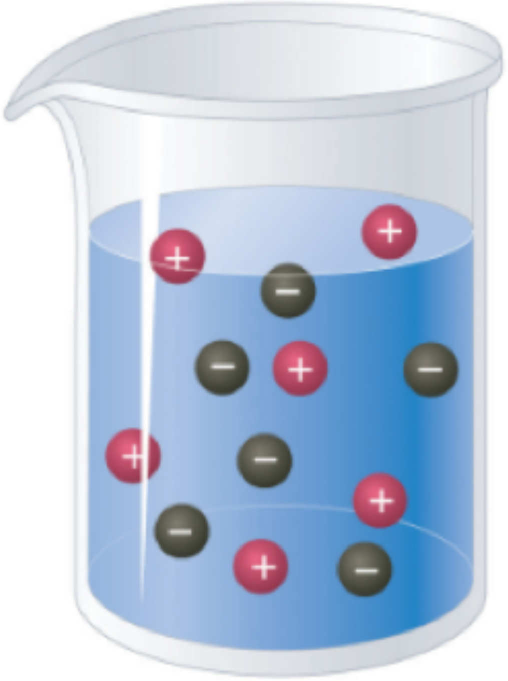
$\text{mmol/l} = \text{ppm} \cdot (\text{density of sample})/(\text{gram formula weight}).$

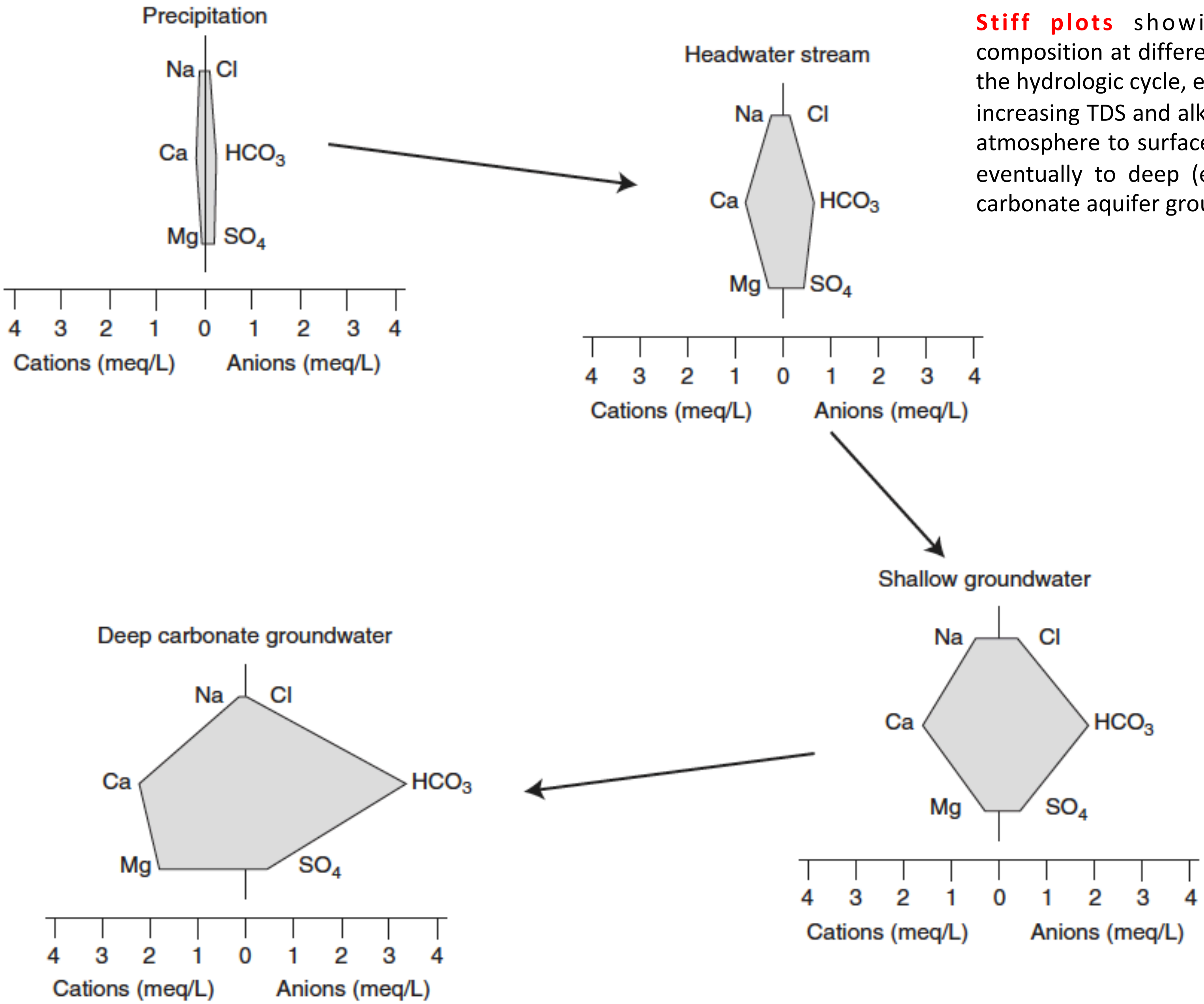
$\text{mmol/l} = \text{meq/l} \,/\, (\text{charge of ion}).$

$$\text{mmol/l} = \text{molality M} \cdot \text{density} \cdot \frac{(\text{weight solution} - \text{weight solutes})}{(\text{weight solution})} \cdot 1000$$



Stiff diagram of water dominated by dissolved Ca, Mg and bicarbonate.





Stiff plots showing water composition at different stages in the hydrologic cycle, emphasizing increasing TDS and alkalinity from atmosphere to surface water and eventually to deep (e.g. 150 m) carbonate aquifer groundwater.

Concentrations of gases

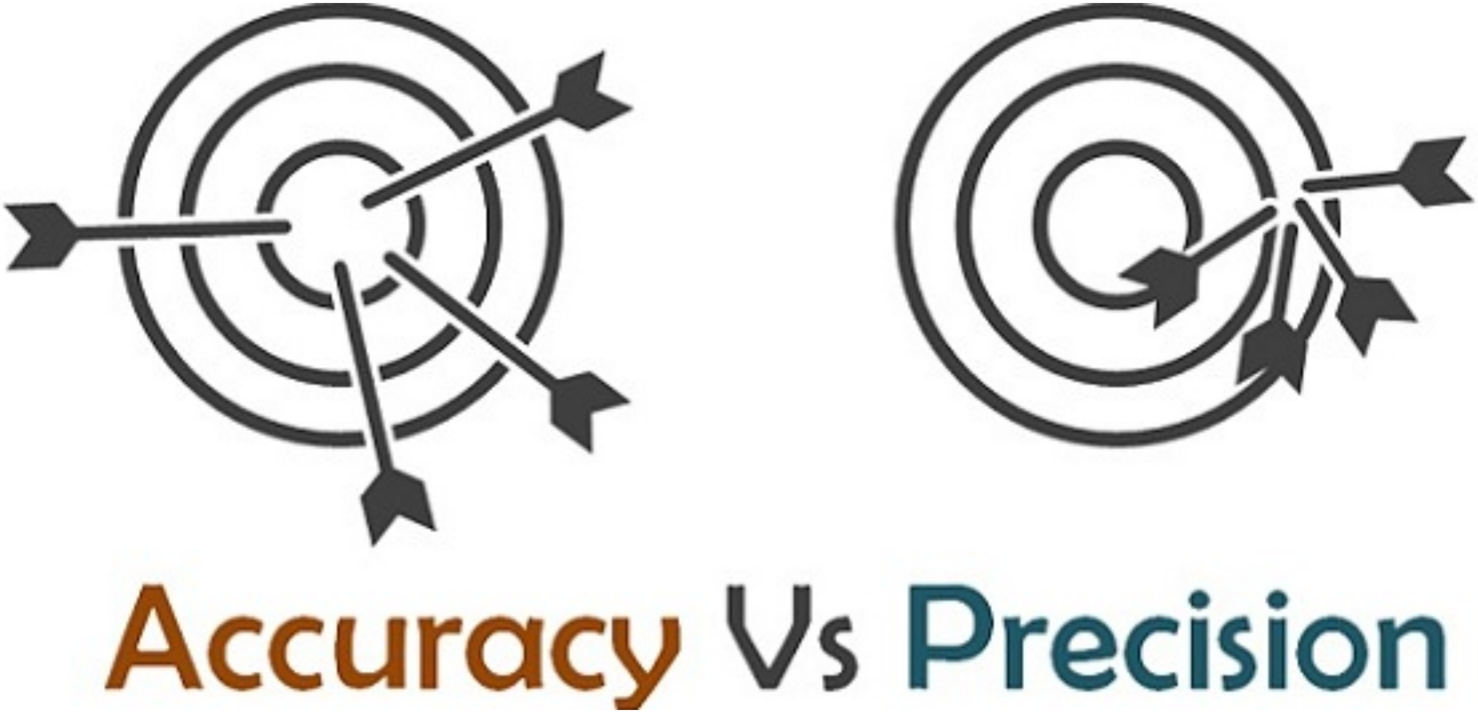
Atmospheric gas concentrations are typically expressed as the proportion of the total volume accounted for by a given gas. For example, the current atmospheric concentration of CO_2 is $\sim$400 ppmv, indicating that 400 out of every one million molecules of gas in Earth's atmosphere is CO_2. At the onset of the industrial revolution atmospheric CO_2 was 280 ppmv.

Less-abundant gases are often expressed in terms of ppbv or pptv (parts per billion or trillion, volumetrically), and the major components of the atmosphere like the fixed gases N_2, O_2 and Ar, are expressed in terms of percent (by vol): $N_2 = 78.1\%$, $O_2 = 20.9\%$ and $Ar = 0.9\%$ (the amounts vary depending on the amount of H_2O vapor in the air, which can range from 0 to 4% by volume). Expressed in this way, CO_2 comprises approximately 0.0400% percent of the atmosphere (vol%), but clearly units of ppmv are more useful for a gas like CO_2.

Gases also dissolve in liquids, and units of concentration in these cases are commonly mg/L or mmol/L.

Notes on precision and accuracy, significant figures and scientific notation

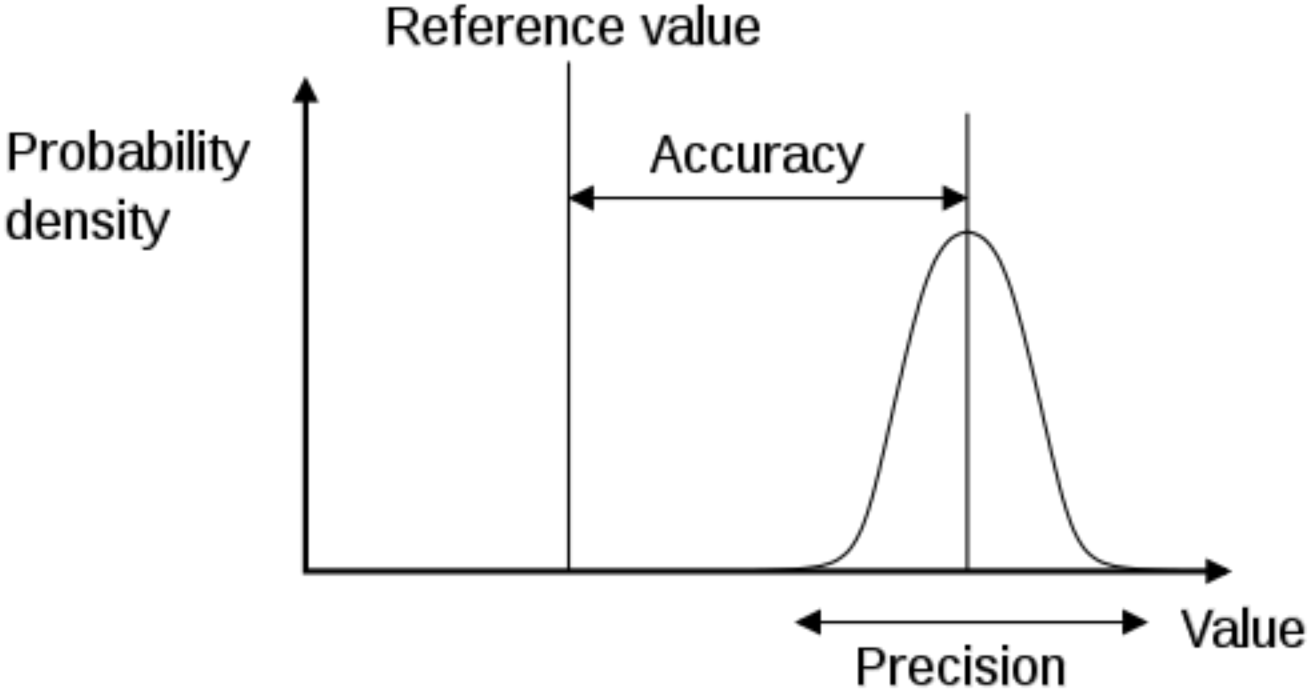
A few important topics related to data analysis and presentation of results are encompassed by the concepts of precision and accuracy.



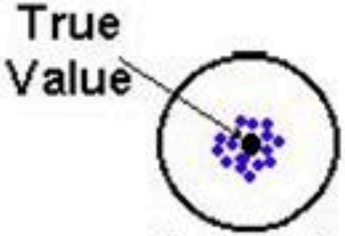
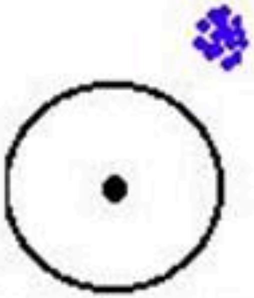
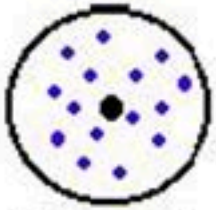
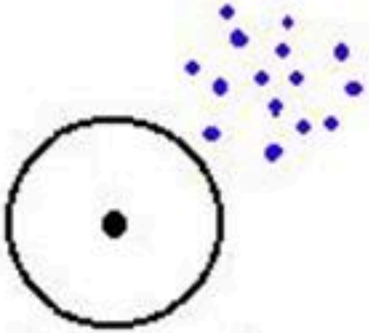
accuracy describes how closely a measured value agrees with the actual value. The accuracy of chemical analyses can be tested by analyzing standards of known concentration. Consider a certified standard solution that contains 250 mg/L of aluminum (Al), and five analyses of this standard on your spectrometer produces results of 237, 271, 244, 262, and 240 mg/L. The mean of those five values is 251 mg/L – the average value is very close to the certified value of 250 mg/L.

One way to express the accuracy of this test is as a percent difference from the certified value:

$$[(251\,\mathrm{mg/L} - 250\,\mathrm{mg/L}) \div 250\,\mathrm{mg/L}] * 100 = 0.4\%$$



However, the five results are somewhat lacking in **precision**, which is basically a measure of the reproducibility of results – how closely do measured results agree with each other? It is conceivable to produce results with a high degree of precision that are lacking in accuracy. For example, after recalibrating the spectrometer and re-analyzing the Al standard, values now are 277, 281, 274, 278 and 275 mg/L. The mean value of 277 mg/L is farther from the certified value of 250 mg/L (the difference from the certified value is 10.8%), but the results are definitely more precise.

		Accuracy	
		Accurate	Not Accurate
Precision	Precise	 **Accurate & Precise**	 **Not Accurate & Precise**
	Not Precise	 **Accurate & Not Precise**	 **Not Accurate & Not Precise**

One way to calculate uncertainty is to determine the standard deviation of the data.

$$s_x = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$$

$n =$ The number of data points

$\bar{x} =$ The mean of the x_i

$x_i =$ Each of the values of the data

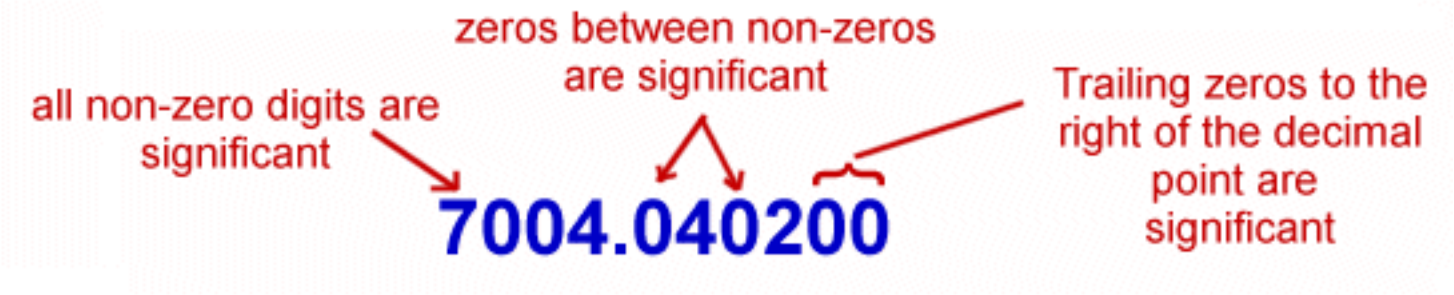
For the values 237, 271, 244, 262 and 240 mg/L,

$\sigma = 14.9$

For the values 277, 281, 274, 278 and 275 mg/L,

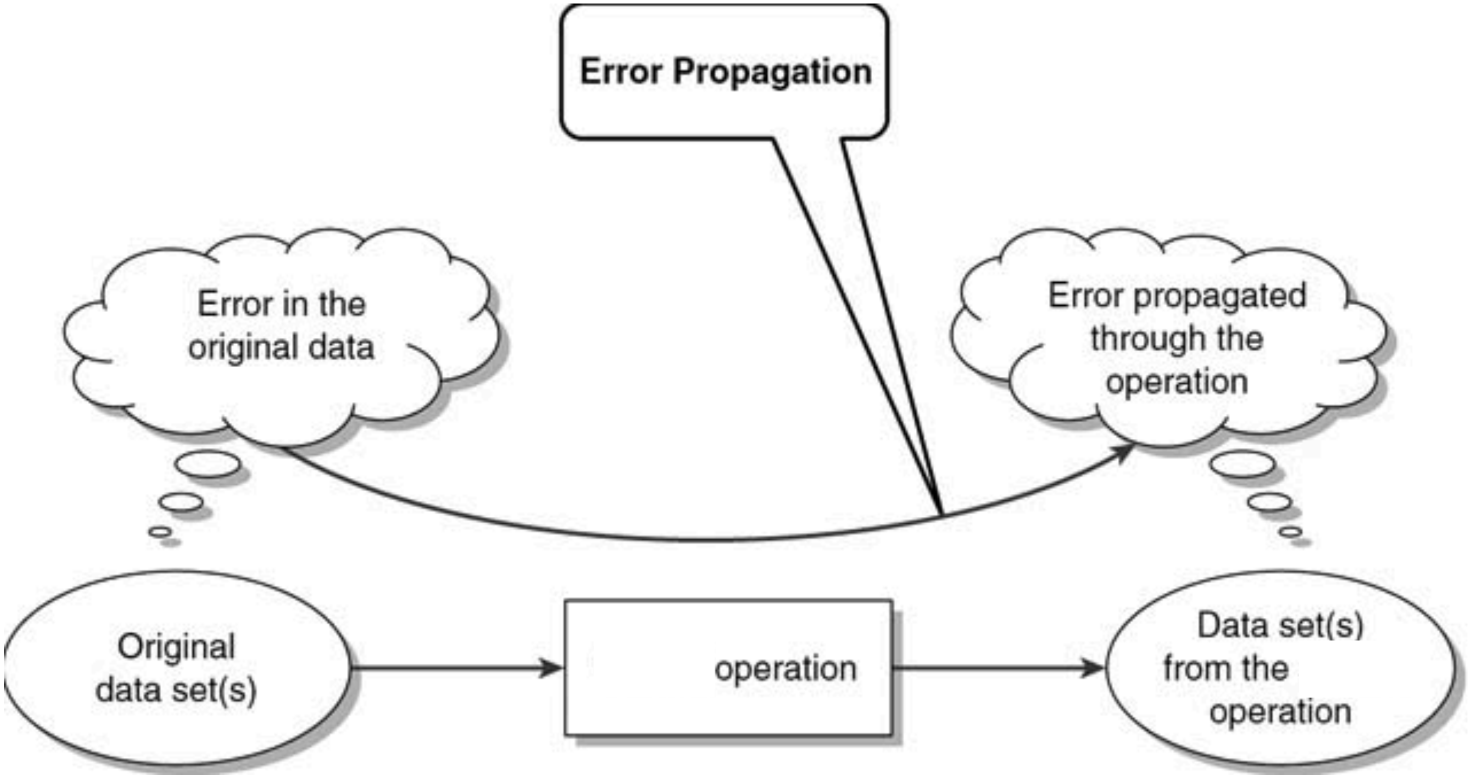
$\sigma = 2.74$

In addition to quantifying uncertainty, it is very important to present numerical results in a manner that relates to the sensitivity of the measurement, or the degree of confidence associated with that measurement, while also trying to avoid propagation of error. Every measurement has some limited number of **significant digits** (or **significant figures**).



Measurements of pH made using litmus paper can only be reported to 1 significant figure (e.g. pH = 6), whereas measurements made with well-calibrated probes may be reported to 3 significant figures (e.g. pH = 5.87).

As a rule, calculations should be carried out using all figures with each of their representative significant figures, and then the final result should be rounded at the end of the calculation.



Using an example where the average concentration of uranium in groundwater in an aquifer is 14.3 μg/L, the aquifer volume is $1.241 \times 10^8\,\text{m}^3$ and average porosity (and thus % water in the saturated zone) is 18%, the resulting mass of U in the aquifer is:

$$14.3\mu g/\text{L} * 1.241 \times 10^8 \text{m}^3 * 1000\,\text{L}/\text{m}^3 * 0.018 \\ = 3.2 \times 10^{11} \mu g\,\text{U}$$

The final result is limited by the two significant figures in 18% (note that conversions involving liters to cubic meters, cm^3 to mL, etc. do not limit sig figs).

Summary of rules for propagation of uncertainty

Function	Uncertainty	Function[a]	Uncertainty[b]
$y = x_1 + x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = x^a$	$\%e_y = a\%e_x$
$y = x_1 - x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = \log x$	$e_y = \frac{1}{\ln 10}\frac{e_x}{x} \approx 0.434\,29\,\frac{e_x}{x}$
$y = x_1 \cdot x_2$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = \ln x$	$e_y = \frac{e_x}{x}$
$y = \frac{x_1}{x_2}$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = 10^x$	$\frac{e_y}{y} = (\ln 10)e_x \approx 2.302\,6\,e_x$
		$y = \mathrm{e}^x$	$\frac{e_y}{y} = e_x$

Also important to understand is the significance of zeros. Consider the following values: 7200, 700043, 0.0436, 0.043600. How many significant figures are reported for each, and why?

- 7200 is assumed to have 2 significant figures because any zero at the end of a number *and before a decimal point* is assumed to not be significant. How many significant figures does 847 000 possess? Three. 7200.0 contains 5 significant figures.

- 700 043 has 6 sig figs. Any zeros within a number are significant.
- 0.0436 has 3 sig figs because any zeros after a decimal point and before the first non-zero digit are not significant.
- 0.043600 has 5 significant figures because zeros that follow a non-zero digit after a decimal point are considered significant (as in 7200.0 example above).

Some of these examples serve to illustrate why scientists tend to express values in terms of **scientific notation**. Using scientific notation, the values above become:

7.2×10^{3} (2 sig figs)

7.2000×10^{3} (if we needed to report 7200 to 5 sig figs, this is how it would look)

7.00043×10^{5} (6 sig figs)

4.36×10^{-2} (3 sig figs)

4.3600×10^{-2} (5 sig figs)