

HANDBOOK OF USEFUL INFORMATION

A. SI Units

Many symbols and units have developed to express physical and chemical quantities. In this course, we will usually use SI (Standard International) symbols and units as they are the most accepted. Some of the SI units are listed below and you should become familiar with them.

Name	Symbol	Quantity
meter	m	length
kilogram	kg	mass
time	s	time
ampere	A	electric current
Kelvin	K	temperature
mole	mol	amount of substance
ohm	Ω	electrical resistance
liter	L	volume
volt	V	electric potential difference

Some of the above units are inconvenient to use in certain situations because the numerical value of the quantity is very large or small. For these situations, decimal multiples and decimal fractions of SI units are used. These are indicated by using the following prefixes in front of the SI symbol.

da = deka = 10^1	(e.g., dag = dekagram = ten grams)
h = hecta = 10^2	(e.g., hg = hectagram = hundred grams)
k = kilo = 10^3	(e.g., kg = kilogram = thousand grams)
M = mega = 10^6	(e.g., $M\Omega$ = megaohm = million ohms)
G = giga = 10^9	(e.g., GL = gigaliter = billion liters)
d = deci = 10^{-1}	(e.g., dL = deciliter = 0.1 liter)
c = centi = 10^{-2}	(e.g., cm = centimeter = 0.01 meter)
m = milli = 10^{-3}	(e.g., mL = milliliter = 0.001 liter)
μ = micro = 10^{-6}	(e.g., μ L = microliter = 10^{-6} liter)
n = nano = 10^{-9}	(e.g., ng = nanogram = 10^{-9} gram)
p = pico = 10^{-12}	(e.g., pmol = picomole = 10^{-12} mole)
f = femto = 10^{-15}	(e.g., fmol = femtomole = 10^{-15} mole)

B. Concentrations

The concentration of a substance in a solution may be expressed in many ways, and it is often necessary to convert from one nomenclature to another. For most of the course we will use the following recommended units.

Recommended Concentration Units

1. **Molarity** - The molarity is the number of moles of substance per liter of solution and has the symbol M with units of mol/L.
2. **Mass per unit volume** - This is the mass of a substance per unit volume of solution. The symbol and units are the same and depend upon the units used to express the mass and volume. The most common ways are given below:

g/L	= grams per liter
mg/L	= milligrams per liter
µg/L	= micrograms per liter
ng/L	= nanograms per liter
g/mL	= grams per milliliter
µg/mL	= micrograms per milliliter
ng/mL	= nanograms per milliliter
pg/mL	= picograms per milliliter
fg/mL	= femtograms per milliliter

Other Concentrations Units You May Encounter

Many other concentration units are employed but in general are not recommended. You should be able to use them and convert them to the recommended units.

1. **Percent** - This concentration unit is not usually recommended because it can be ambiguous. Strictly speaking, a concentration in percent is the ratio of the amount of the substance to the amount of solution times one hundred where the amounts are expressed in the same units. The amount can be expressed as a mass or a volume so this must also be specified to avoid confusion. The following means of expression are often used.

a. **Volume percent** - % (v/v)

(mL of substance per mL of solution) x 100 or mL of substance per 100 mL of solution (mL/dL)

b. **Weight percent** - % (w/w)

(g of substance per g of solution) x 100 or g of substance per 100 g (g/hg)

Weight percent is also used to express the amount of substance or analyte in a sample. Thus a rock that contains 1% (w/w) Ca contains 0.01 g of Ca per g of rock.

c. **Weight/volume percent** % (w/v)

This unit is widely used but is controversial because a percentage formally has no units (i.e., the units of the numerator and denominator should be the same so the units cancel out). The most common units for % (w/v) are g/100 mL or g/dL. For dilute aqueous solutions where 1 mL of solution has a mass of about 1 g, % (w/v) approximates the % (w/w) concentration.

The % concentrations units are most useful for expressing the concentration of solutions where the exact concentration is not critical. For example a 10% (v/v) solution of nitric acid (HNO_3) may be used as a rinsing solution where the exact concentration is not critical (i.e., 8 - 12% (v/v) acceptable). This solution is prepared by diluting about 10 mL of HNO_3 to 100 mL with water. If you see a concentration expressed as a % without a v/v, w/w, or w/v then the unit is ambiguous although usually it means a % (w/w).

2. **Parts per units** - The following units are sometimes used although their use is discouraged because they are ambiguous.

a. **ppt** - parts per thousand meaning "grams per thousand mL" (preferred units would be mg/mL or g/L)

b. **ppm** - parts per million meaning "grams per million mL" (preferred units would be $\mu\text{g}/\text{mL}$, or mg/L)

c. **ppb** - parts per billion meaning "grams per billion mL" (preferred units would be ng/mL, or $\mu\text{g}/\text{L}$)

d. **ppttr** - parts per trillion meaning "grams per trillion mL" (preferred units would be pg/mL, or ng/L)

The problem with these units is the same as with percentage. Strictly speaking a solution or sample that is 1 ppm in a substance contains 1 part of the substance in a million parts of total

solution or sample. Formally the "part" should be in the same units (mass or volume) which is not the way ppm is usually defined. Since 1 mL of water has a mass of 1 g at 4°C, a ppm expressed as $\mu\text{g/mL}$ is equivalent to a $\mu\text{g/g}$ in a dilute aqueous solution. When you see the "part per" unit, a warning flag should go up. For an **aqueous** solution **1 ppm** usually means one gram of substance in a million mL of solution or, since there is usually not as much as a million mL, one **μg of substance per mL of solution**. In a **solid** sample, 1 ppm usually means **1 μg of substance per g of sample**, while in an air sample it usually means **1 μL of substance per L of air**.

Although not usually done, we will attempt to put w/w, v/v, or w/v after the part per units. Thus 1 ppm (w/v) = 1 $\mu\text{g/mL}$.

3. **Normality** is the number of equivalents per L and will not be used in this course.
4. **Mole fraction** is the moles of a substance divided by the total number of moles of solution (including solvent) and will not be used in this course.
5. For solid samples it is acceptable to use mass-mass units since the volume may be difficult to determine. However, units of $\mu\text{g/g}$ or ng/g are preferred to ppm (w/w) or ppb (w/w), respectively. Weight % is a specific case of this.
6. **Molality** is the number of moles of a substance per 1000 g of solvent.

One must be careful to clearly designate the exact substance in the above definitions. Consider a solution of sulfuric acid, H_2SO_4 .

1. The molarity of H_2SO_4 and SO_4^{2-} are the same and half the molarity of H^+ .
2. A solution 1 $\mu\text{g/mL}$ or 1 ppm (w/w) in S would be

$$\frac{32 + 4 \cdot 16}{32} \cdot 1 = \frac{96}{32} = 3 \mu\text{g/mL in } \text{SO}_4^{2-}$$

C. Wavelength Specification

The accepted wavelength unit for analytical UV-visible spectroscopy is the **nanometer** = nm = 10^{-9} m.

However two other units are commonly used:

angstrom = Å = 10^{-10} m = 10^{-8} cm = 0.1 nm (not a favored unit)

micrometer = μm = 10^{-6} m = 10^3 nm = 10^4 Å

picometer = pm = 10^{-12} m = 10^{-3} nm

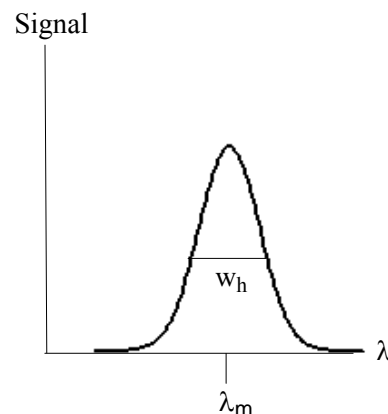
In some literature, the term micron with the symbol μ is used to mean micrometer. The term “micron” is not recommended.

2. For infrared work, either the micrometer (μm) or wavenumber ($\bar{\nu}$ in cm^{-1}) are used to specify wavelength

$$\bar{\nu} = 1/\lambda \text{ for } \lambda \text{ in cm, } \quad \bar{\nu} = 10^7/\lambda \text{ for } \lambda \text{ in nm, } \quad \text{or} \quad \bar{\nu} = 10^3/\lambda \text{ in } \mu\text{m}^{-1}$$

D. Peak specifications

In spectrometric methods, a spectrum is a plot of instrumental response versus wavelength. It is often used to determine at which wavelengths the desired information can be found. The spectrum usually consists of one or more peaks which may or may not be resolved from each other. The characteristics of a given peak are indicated by specification of the wavelength of maximum instrumental response (λ_m) and the **half-width** of the peak.



Note that the half-width (w_h) is the width of the peak at half its maximum height. It is sometimes called the full width at half maximum (FWHM). The magnitude of the half-width may depend on just what is plotted. The “signal” in the figure above is usually transmittance (T) or absorbance (A) for absorption techniques and photocurrent voltage (E_p) for emission or luminescence techniques.

The symbol λ_0 will be used to specify the wavelength setting of a monochromator or the wavelength setting for maximum transmittance of an absorption band or interference filter.

E. Accuracy and Precision

Accuracy - the nearness of a measurement to its correct value

Precision - the reproducibility of a measurement

- If one makes n measurements of the quantity X_i , the **mean** is given by

$$\bar{X} = \sum_{i=1}^n X_i/n$$

In this course,

- The **absolute error** is defined as $\bar{X} - \mu$ where \bar{X} is the experimental mean and μ is the true value (population mean).
- The **relative error** is defined as $(\bar{X} - \mu)/\mu$ and often expressed as a percent:

$$\%error = 100 \times |experimental\ value - true\ value| / true\ value.$$

Note that the “**true**” value in the above definitions is often called the **expected value**, the **nominal value**, or the **theoretical value** depending on the situation.

- The term **experimental error** can have different meanings, and we will normally use the absolute or relative error as defined above. Most commonly an expression such as “calculate the relative error” will be used in experiments where a quantity is measured and we wish to compare it to an expected value that is either given or calculated.
- The **precision** is inversely related to the **standard deviation**. The experimental standard deviation s is found from

$$s = \left[\sum_{i=1}^n (X_i - \bar{X})^2 / (n - 1) \right]^{1/2}$$

and is an estimate of the population standard deviation, σ .

- The **relative standard deviation (RSD)** is s/\bar{X} . The RSD is often used as a quantitative expression of the precision.

F. Propagation of Error (Uncertainty) (background material necessary for exp. 1A)

If a result R is computed from or is dependent on a number of independent measurements or variables (A,B,C...), the error in R can be estimated from the known errors in A, B, C,... with propagation of error mathematics. Thus if,

$$R = f(A, B, C...) \quad (2)$$

$$\Delta R = \left| \frac{\partial R}{\partial A} \right| \Delta A + \left| \frac{\partial R}{\partial B} \right| \Delta B + \left| \frac{\partial R}{\partial C} \right| \Delta C + \dots \quad (3)$$

where ΔR , ΔA , ΔB , and ΔC are maximum absolute errors in R, A, B, and C, respectively. Note that the derivatives are first evaluated (they may be negative) then the absolute value is taken.

If one is concerned with random errors, then equation 3 can be written as

$$s_R = \left[\left(\frac{\partial R}{\partial A} \right)^2 s_A^2 + \left(\frac{\partial R}{\partial B} \right)^2 s_B^2 + \left(\frac{\partial R}{\partial C} \right)^2 s_C^2 + \dots \right]^{1/2} \quad (4)$$

where s_R , s_A , s_B , and s_C are the standard deviations in R, A, B, and C, respectively. In equations 3 and 4, it is assumed that errors or standard deviations are much smaller than the mean values (e.g., $\Delta A \ll A$, $s_A \ll A$). **Note that Equation 3 should be used for Experiment 1A, Electronic Instrumentation, since the tolerance of components is a specification of maximum absolute error.**

Note that **propagation of error mathematics** is used to **estimate the expected experimental error** which is different from **calculating the relative experimental error** (p. 6) after conducting the experiment, using

$$\% \text{ relative experimental error} = 100 \times \frac{|\text{true value} - \text{experimental value}|}{\text{true value}}$$

A measured experimental error that is less or equal to the expected error calculated from propagation of error mathematics suggests that the factors that determine the uncertainty are well understood.

Formulas for random errors for some common functions are listed below (and $s_R = \sigma_R$).

$$1. \quad R = A \pm B \quad (5)$$

$$\sigma_R = (\sigma_A^2 + \sigma_B^2)^{1/2} \quad (6)$$

$$2. \quad R = A \times B \quad (7)$$

$$\sigma_R = (B^2 \sigma_A^2 + A^2 \sigma_B^2)^{1/2} \quad (8)$$

$$\frac{\sigma_R}{R} = \left[\left(\frac{\sigma_A}{A} \right)^2 + \left(\frac{\sigma_B}{B} \right)^2 \right]^{1/2} \quad (9)$$

$$3. \quad R = A/B \quad (10)$$

$$\frac{\sigma_R}{R} = \left[\left(\frac{\sigma_A}{A} \right)^2 + \left(\frac{\sigma_B}{B} \right)^2 \right]^{1/2} \quad (11)$$

$$4. \quad R = \log 10A = (0.4343) \ln A \quad (12)$$

$$\sigma_R = (0.4343) \sigma_A / A \quad (13)$$

$$5. \quad R = e^A \quad (14)$$

$$\sigma_R = e^A \sigma_A = R \sigma_A \quad (15)$$

$$6. \quad R = \frac{A - C}{B - C} \quad (16)$$

$$\sigma_R = R \left[\frac{\sigma_A^2}{(A - C)^2} + \frac{\sigma_B^2}{(B - C)^2} + \left(\frac{1}{A - C} + \frac{1}{B - C} \right)^2 \sigma_C^2 \right]^{1/2} \quad (17)$$

$$\sigma_R = R \left[\frac{\sigma_A^2}{(A - C)^2} + \frac{\sigma_B^2}{(B - C)^2} + \left(\frac{1 - R}{R} \right)^2 + \frac{\sigma_C^2}{(B - C)^2} \right]^{1/2} \quad (18)$$

$$\sigma_R = \frac{R}{(B - C)} \left[\frac{\sigma_A^2}{R^2} + \sigma_B + \left(\frac{1 - R}{R} \right)^2 \sigma_C^2 \right]^{1/2} \quad (19)$$

Example for estimating systematic relative and absolute errors:

Calculate the expected relative systematic error in the voltage drop across a 100 Ω resistor with 1% tolerance with a current of 1.00 mA as measured with a multimeter with 1% accuracy.

$$E = IR = 10^{-3} \text{ A} \times 10^2 \Omega = 0.100 \text{ V}$$

$$dE = R dI + I dR$$

Divide by E

$$dE/E = (R/E) dI + (I/E) dR$$

Substitute IR for E

$$dE/E = dI/I + dR/R$$

Replace the differentials by absolute errors

$$\Delta E/E = \Delta I/I + \Delta R/R$$

Note that whenever a quantity is a product and/or quotient of two or more variables, the relative systematic error in the quantity is the sum of the relative errors in each of the variables. For this problem,

$$\Delta I/I = 1\% \text{ and } \Delta R/R = 1\% \text{ and thus } \Delta E/E = 1\% + 1\% = 2\%$$

The maximum relative error is 2% and the maximum absolute error is $0.100 \text{ V} \times 2\% = 0.002 \text{ V}$.

For more discussion of statistics and propagation of error:

1. Shoemaker, D. P., Garland, and Nibler, J. W. Experiments in Physical Chemistry, 6th ed. pp 55-61, McGraw-Hill, New York, 1996 (or 9th ed. 2017).
2. Harris, D. C., "Quantitative Chemical Analysis", any addition, Freeman and Co, 2006-2018.
3. National Bureau of Standards, Special Publication 300, vol. 1, "Precision Measurement and Calibration". <https://ia902501.us.archive.org/7/items/precisionmeasure3001kuha/precisionmeasure3001kuha.pdf> (very large file), see pp. 331-341, 1969. (Accessed 9/29/19)
4. Eric Weisstein's World of Mathematics, <http://mathworld.wolfram.com/>© 1996-2019, Eric W. Weisstein and Wolfram Research, Inc. "Web's most extensive mathematical resource, provided as a free service to the world's mathematics and internet communities as part of a commitment to education and educational outreach by Wolfram Research, makers of Mathematica."