Analytical Chemistry

Ch. 1 & 2

Chemical Measurements
Tools of the Trade

Ch. 1

1) units of measurement

2) chemical concentrations

SI units of measurement

See Table 1-1

Table 1-2 lists some quantities that are defined in terms of the fundamental quantities.

See Table 1-2

Prefixes as Multipliers

Rather than using exponential notation, we often use prefixes from Table 1-3 to express large or small quantities

$$1.7 \times 10^4 \cancel{\text{m}} \times \frac{1 \text{ km}}{10^3 \cancel{\text{m}}} = 1.7 \times 10^1 \text{ km} = 17 \text{ km}$$

See Table 1-3

Converting Between Units

Although SI is the internationally accepted system of measurement in science, other units are encountered.

Useful conversion factors are found in the next slide

See Table 1-4

9e offers the same table, but less organized

Chemical Concentrations

- A **solution** is a homogeneous mixture of two or more substances
  : **solute** (minor) + **solvent** (major)

- Two types of solutions
  1) **aqueous solutions**: solvent is water
  2) **non-aqueous solutions**: solvent is not water

- **Concentration**: how much solute is contained in a given volume or mass of solution or solvent
  : denoted with square brackets
  → "[H^+]" means "the concentration of H^+."

Chemical Concentrations

Molarity and Molality

Molarity (M): the number of moles of a substance per liter of solution.

Molality (m): moles of substance per kilogram of solvent (not total solution).

$$\text{Molarity (M)} = \frac{\text{moles of solute (mol)}}{\text{volumes of solution (L)}} \qquad \text{(dependent on } T\text{)}$$

$$\text{Molality (m)} = \frac{\text{moles of solute (mol)}}{\text{mass of solvent (kg)}} \qquad \text{(independent of } T\text{)}$$

Molality (m): independent of temperature.

Molarity (M): changes with temperature because the volume of a solution usually increases when it is heated

Percent Composition

- The percentage of a component in a mixture or solution is usually expressed as a weight percent (wt%):

$$\text{Weight percent} = \frac{\text{mass of solute}}{\text{mass of total solution or mixture}} \times 100$$

Example) A common form of ethanol is 95 wt%;

→means 95 g of ethanol per 100 g of total solution.

the remainder is water.

- Volume percent (vol%) is defined as

$$\text{Volume percent} = \frac{\text{volume of solute}}{\text{volume of total solution}} \times 100$$

Parts per Million and Parts per Billion

ppm, ppb (parts per million, billion)

Sometimes composition is expressed as parts per million (ppm) or parts per billion (ppb)

→ mean grams of substance per million or billion grams of total solution or mixture.

$$\text{ppm} = \frac{\text{weight of substance (kg)}}{\text{total weight of sample (kg)}} \times 10^6 \ \ (\text{mg/kg}) \approx 1\mu\text{g/mL} = 1\text{mg/L}$$

$$\text{ppb} = \frac{\text{weight of substance (kg)}}{\text{total weight of sample (kg)}} \times 10^9 \ \ (\mu\text{g/kg}) \approx 1\text{ng/mL} = 1\mu\text{g/L}$$

Because the density of a dilute aqueous solution is close to 1.00 g/mL,

→ we frequently equate 1 g of water with 1 mL of water, although this equivalence is only approximate.

For **gases**,

ppm usually refers to volume rather than mass.

Example) Atmospheric CO_2 has a concentration near 380 ppm,

→ means 380 μL CO_2 per liter of air.

→ ex) 미세먼지 in μg / m^3

Electrolyte

- An electrolyte is a substance that dissociates into ions in solution.
- In general, electrolytes are more dissociated in water than in other solvents.
- We refer to a compound that is mostly dissociated into ions as a **strong electrolyte**.

One that is partially dissociated is called a **weak electrolyte**.

2-4. Burets

A precisely manufactured glass tube to measure the volume of liquid delivered through the stopcock at the bottom.

See Fig 2-8

<u>Operating a buret</u>

- wash buret with new solution
- eliminate air bubble before use
- drain liquid slowly
- deliver fraction of a drop near end point
- read bottom of concave meniscus
- estimate reading to 1/10 of a division
- avoid parallax error
- account for graduation thickness in readings

See Fig 2-9

[Reference]

2-5. Volumetric Flasks

TC: To contain a particular volume of solution at $20^{O}C$.

- TC = to contain (volumetric flasks)
- TD = to deliver (pipets and burets)

See Fig 2-11

To reduce adsorption of cations on the glass surface

- washing with acid: replacing cations on the glass surface with H^+
- plastic (polypropylene) flask for trace analysis

2-6. Pipets and Syringes

delivery of known volumes of liquid

- transfer pipet : the last drop should not be blown out
- measuring (Mohr) pipet : to deliver a variable volume (by difference)

See Fig 2-12

[Reference]

Comparison of tolerances of measuring tools

See Table 2-2, 2-3, 2-4

2-6. Pipets and Syringes

How to transfer pipet

- rubber bulb : not your mouth!
- discard one or two pipet volumes of liquid to rinse traces of previous reagents from the pipet
- touch the tip of the pipet to the side of a beaker -> calibration mark -> transfer/drain -> holding the tip against the wall of the vessel -> do not blow out the last drop
- rinse with distilled water : not to dry inside of a pipet

[Reference]

2-6. Pipets and Syringes

Micropipets

- delivering volumes of 1 to 1000 μL : disposable PP tip
- do not contaminate the disposable tip : package/dipenser
- set the volume → depress the plunger → hold pipet vertically, dip it 3-5 mm → slowly release the plunger to suck up liquid → transfer → touch the tip to the wall of the receiver → gently depress the plunger → depress the plunger further to squirt out the last liquid
- The volume of liquid depends on the angle and depth.

See Fig 2-14

Syringe

- discard several volumes of liquid : to wash the glass wall and to remove air bubble from the barrel
- steel needle is attacked by strong acid

[Reference]

2-7. Filtration

See Fig 2-17

2-7. Filtration

See Fig 2-18, 19

Analytical Chemistry

Ch. 3

Experimental Errors

Chapter 3. Experimental Error

- There is **error** associated with every measurement.
- There is no way to measure the "true value" of anything.

→ The best we can do in a chemical analysis is to carefully apply a technique whose experience tells us is reliable.

- **Repetition** of one method of measurement several times tells us the **precision** (reproducibility) of the measurement.
- If the results of measuring the same quantity by different methods agree with one another,

→ then we become confident that the results are accurate

→ means they are near the "true" value.

3-1. Significant Figures

- The number of **significant figures**

→ the minimum number of digits needed to write a given value in scientific notation without loss of **accuracy**.

- For examples:

The number 142.7 has four significant figures

→ It can be written as 1.427×10^2.

- If you write $1.427\,0 \times 10^2$,

→ is not the case for the number 142.7

→ The number $1.427\,0 \times 10^2$ has five significant figures.

→ you imply that you know the value of the digit after 7

- The number 6.302×10^{-6} has four significant figures

→ You could write the same number as 0.000 006 302

→ The zeros to the left of the 6 are merely holding decimal places.

- The number 92 500 is ambiguous.

→ It could mean any of the following:

9.25×10^4	3 significant figures
9.250×10^4	4 significant figures
$9.250\,0 \times 10^4$	5 significant figures

- Zeros are significant when they occur (1) in the middle of a number or (2) at the end of a number on the right-hand side of a decimal point.

- The last significant digit (farthest to the right) in a measured quantity always has some associated uncertainty.

- The scale of a Spectronic 20 spectrophotometer is drawn in Figure 3-1.
- The needle in the figure appears to be at an absorbance value of 0.234.

→We say that this number has three significant figures because the numbers 2 and 3 are completely certain and the number 4 is an estimate.

→ The value might be read 0.233 or 0.235 by other people.

See Fig 3-1

3-2. Significant Figures in Arithmetic

- We now consider how many digits to retain in the answer after you have performed arithmetic operations with your data.

→ Rounding should only be done on the final answer (not intermediate results), to avoid accumulating round-off errors.

1) Addition & Substraction

- If the numbers to be added or subtracted have equal numbers of digits,

→ the answer goes to the same decimal place as in any of the individual numbers:

$$\begin{array}{r} 1.362 \times 10^{-4} \\ + \ 3.111 \times 10^{-4} \\ \hline 4.473 \times 10^{-4} \end{array}$$

- The number of significant figures in the answer may exceed or be less than that in the original data.

$$\begin{array}{r} 5.345 \\ +\ 6.728 \\ \hline 12.073 \end{array} \qquad \begin{array}{r} 7.26 \times 10^{14} \\ -\ 6.69 \times 10^{14} \\ \hline 0.57 \times 10^{14} \end{array}$$

- If the numbers being added do not have the same number of significant figures,

→ we are limited by the least-certain one.

$$\begin{array}{lll} & 18.998\,403\,2 & \text{(F)} \\ + & 18.998\,403\,2 & \text{(F)} \\ + & 83.798 & \text{(Kr)} \\ \hline & 121.794\underbrace{\,806\,4}_{\text{Not significant}} & \end{array}$$

$$
\begin{array}{lll}
 & 18.998\,403\,2 & \text{(F)} \\
+ & 18.998\,403\,2 & \text{(F)} \\
+ & 83.798 & \text{(Kr)} \\
\hline
 & 121.794\underbrace{806\,4}_{\text{Not significant}} &
\end{array}
$$

- The digits 806 4 lie beyond the last significant decimal place.
- Because this number is more than halfway to the next higher digit,

→ we round the 4 up to 5

→ that is, we round up to 121.795 instead of down to 121.794

- If the insignificant figures were less than halfway,

→ we would round down.

→ For example, 121.794 3 is rounded to 121.794.

- In the special case where the number is exactly halfway, round to the nearest even digit.

- For examples

43.55 → 43.6 if we can only have three significant figures

1.425×10^{-9} → 1.42×10^{-9} if we can only have three significant figures

- Addition and subtraction:

→ Express all numbers with the same exponent and align all numbers with respect to the decimal point.

→ Round off the answer according to the number of decimal places in the number with the fewest decimal places.

$$\begin{array}{r} 1.632 \times 10^5 \\ +\ 4.107 \times 10^3 \\ +\ 0.984 \times 10^6 \\ \hline \end{array} \quad \rightarrow \quad \begin{array}{rl} 1.632 & \times 10^5 \\ +\ 0.041\,07 & \times 10^5 \\ +\ 9.84 & \times 10^5 \\ \hline 11.51 & \times 10^5 \end{array}$$

Multiplication and Division

- In multiplication and division, we are normally limited to the number of digits contained in the number with the fewest significant figures:

$$\begin{array}{r} 3.26 \times 10^{-5} \\ \times\ 1.78 \qquad\quad \\ \hline 5.80 \times 10^{-5} \end{array} \qquad \begin{array}{ll} \quad 4.317\,9 & \times\ 10^{12} \\ \times\ 3.6 & \times\ 10^{-19} \\ \hline \quad 1.6 & \times\ 10^{-6} \end{array} \qquad \begin{array}{r} 34.60 \\ \div\ 2.462\,87 \\ \hline 14.05 \end{array}$$

Logarithms and Antilogarithms

- The base 10 logarithm of n is the number a, whose value is such that $n=10^a$:

Logarithm of n: $$n = 10^a \quad \text{means that} \quad \log n = a$$

- In Equation 3-1,

→ the number n is said to be the antilogarithm of a.

→ That is, the antilogarithm of 2 is 100 because $10^2 = 100$

→ the antilogarithm of -3 is 0.001 because $10^{-3} = 0.001$

- A logarithm is composed of a characteristic and a mantissa.

→ the characteristic is the integer part

→ the mantissa is the decimal part

$$\log 339 = \underbrace{2}_{\substack{\text{Characteristic} \\ = 2}}.\underbrace{530}_{\substack{\text{Mantissa} \\ = 0.530}}$$

- The number 339 can be written as 3.39×10^2
- The number of digits in the mantissa of log 339 should equal the number of significant figures in 339.

→ The logarithm of 339 is properly expressed as 2.530.

- The characteristic, 2, corresponds to the exponent in 3.39×10^2

- In the conversion of a logarithm into its antilogarithm,

→ the number of significant figures in the antilogarithm should equal the number of digits in the mantissa.

→ Thus,

$$\text{antilog}\,(-3.\underbrace{42}_{\text{2 digits}}) = 10^{-3.\underbrace{42}_{\text{2 digits}}} = \underbrace{3.8}_{\text{2 digits}} \times 10^{-4}$$

- Here are several examples showing the proper use of significant figures:

$$\log 0.001\,237 = -2.907\,6 \qquad \text{antilog}\; 4.37 = 2.3 \times 10^{4}$$

$$\log 1\,237 = 3.092\,4 \qquad 10^{4.37} = 2.3 \times 10^{4}$$

$$\log 3.2 = 0.51 \qquad 10^{-2.600} = 2.51 \times 10^{-3}$$