Chemistry 233

Chapter 3

Experimental Error

Mass = 4.635 ± 0.002 g

Volume = 1.13 ± 0.05 mL

$$d = \frac{m}{v} = 4.1018 \ \pm ? \ \ g/mL$$

Significant Figures

Significant figures: minimum number of digits required to express a value in scientific notation without loss of accuracy.

Scientific Notation

The number of atoms in 12 g of carbon:

602,200,000,000,000,000,000,000

6.022×10^{23}

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The mass of a single carbon atom in grams:

0.0000000000000000000000199

1.99×10^{-23}

$N \times 10^{n}$

N is a number between 1 and 10

n is a positive or negative integer

568.762 6 significant figures

← move decimal left

$n > 0$

$568.762 = 5.68762 \times 10^2$

$15.6 = 1.56 \times 10^1$	3 sig. fgs.
$153.6 = 1.536 \times 10^2$	4 sig. fgs.
$1536.0 = 1.5360 \times 10^3$	5 sig. fgs.

0.00000772

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→ move decimal right

$n < 0$

$0.00000772 = 7.72 \times 10^{-6}$ 3 significant figures

$0.10 = 1.0 \times 10^{-1}$	2 sig. fgs.
$0.0123 = 1.23 \times 10^{-2}$	3 sig. fgs.
$0.0010 = 1.0 \times 10^{-3}$	2 sig. fgs.
$0.0000505 = 5.05 \times 10^{-5}$	3 sig. fgs.

23400 is ambiguous and may have 3 or 4 or 5 sig.fgs.

2.34×10^4 **or** 2.340×10^4 **or** 2.3400×10^4

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.

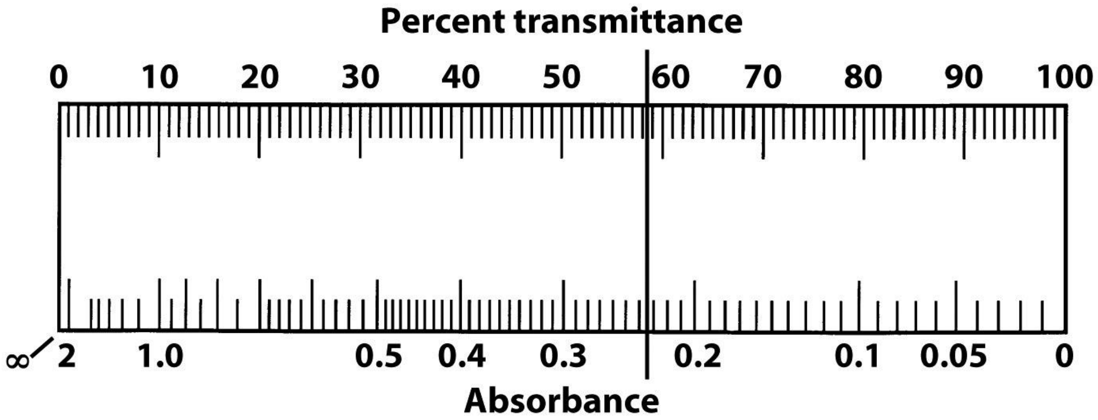

Figure 3-1
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● The last significant digit (farthest to the right) in a measured quantity always has some associated *uncertainty*. The minimum uncertainty is ±1 in the last digit.

Percent transmittance = 58.**3** ± 0.1	3 sig. fgs.
Absorbance = 0.23**4** ± 0.001	3 sig. fgs.

● When reading the scale of any apparatus, try to estimate to the nearest tenth of a division. On a 50-mL burette, which is graduated to 0.1 mL, read the level to the nearest 0.01mL.

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<u>Significant Figures in Arithmetic</u>

Addition and Subtraction

$$
\begin{array}{r}
1.362 \times 10^{-4} \\
+3.111 \times 10^{-4} \\
\hline
4.473 \times 10^{-4}
\end{array}
\qquad
\begin{array}{r}
5.345 \\
+\ 6.728 \\
\hline
12.073
\end{array}
\qquad
\begin{array}{r}
6.21 \\
-\ 5.67 \\
\hline
0.54
\end{array}
$$

When addition or subtraction is performed, answers are rounded to the least significant *<u>decimal place.</u>*

Rounding off Numbers

Rounding off to 5 significant figures**:**

1.3776<u>43</u> $\rightarrow$ **1.3776**

1.3777<u>51</u> $\rightarrow$ **1.3778**

1.3777<u>50</u> $\rightarrow$ **1.3778**

1.3776<u>50</u> $\rightarrow$ **1.3776**

The molecular mass of KrF_2 is known only to the second decimal place, because we only know the atomic mass of Kr to two decimal places:

$$\begin{array}{ll} \ 18.998\,403\,2 & \text{(F)} \\ +\ 18.998\,403\,2 & \text{(F)} \\ +\ 83.80 & \text{(Kr)} \\ \hline \ 121.79\,\boldsymbol{\mathit{6806\ 4}} & \end{array}$$

Not significant

The number 121.796 806 4 should be rounded to 121.80 as the final answer.

$$\begin{array}{l} \ 1.632 \times 10^5 \\ +\ 4.107 \times 10^3 \\ +\ 0.984 \times 10^6 \end{array} \quad \rightarrow \quad \begin{array}{l} \ 1.632 \times 10^5 \\ +\ 0.04107 \times 10^5 \\ +\ 9.84 \times 10^5 \\ \hline 11.51\boldsymbol{\mathit{307}} \times 10^5 \rightarrow 11.51 \times 10^5 \end{array}$$

$\downarrow$

$$\begin{array}{l} \ 0.1632 \times 10^6 \\ +\ 0.004107 \times 10^6 \\ +\ 0.984 \times 10^6 \\ \hline \ 1.151307 \times 10^6 \end{array} \quad \rightarrow \quad 1.151 \times 10^6$$

$$11.51 \times 10^5 = 1.151 \times 10^6$$

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:

7.26×10^{-4}	3.2192×10^{9}	18.44
$\times\ 1.12$	$\times\ 2.4 \times 10^{-19}$	$\div 1.33145$
8.13×10^{-4}	7.7×10^{-10}	13.85

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Logarithms and Antilogarithms

log 339 = 2.530*199698* → 2.530

2 is called characteristic and .530 called mantissa

The number of digits in the mantissa of log 339 should equal the number of significant figures in 339.

$\log 3.39 \times 10^{-5} = 4.470$

$\log 4.3532 \times 10^{-5} = -\ 4.36119$

$\text{antilog}\ (-3.61) = 10^{-3.61} = 2.5 \times 10^{-4}$

$\text{antilog}\ 4.65 = 10^{4.65} = 4.5 \times 10^{4}$

$10^{-3.400} = 3.98 \times 10^{-4}$

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

Types of Error

1) **Systematic error**, also called **determinate error**, arises from a flaw in equipment or the design of an experiment. In principle, systematic error can be discovered and corrected, although this may not be easy.

Example 1) standardization of a pH meter.

Solution	pH reading	Actual pH
Buffer solution	7.00	7.08
Unknown solution	7.31	7.39

● All pH readings will be 0.08 pH unit too **low**.

● This systematic error could be discovered by using a second buffer of known pH to test the meter.

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Example 2) Uncalibrated burette

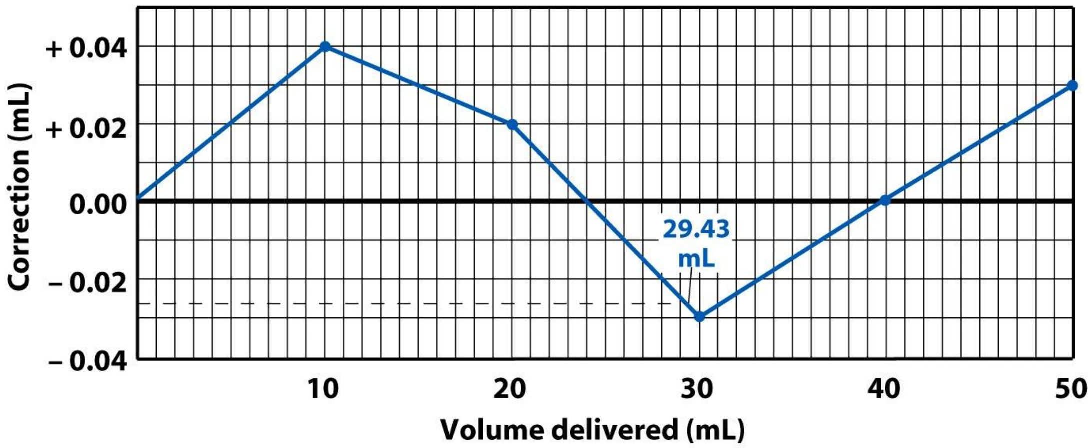

Figure 3-3
Quantitative Chemical Analysis, Seventh Edition

Calibration curve for a 50-mL burette. The volume delivered can be read to the nearest 0.1 mL. If your burette reading is 29.43 mL, you can find the correction factor accurately enough by locating 29.4 mL on the graph. The correction factor on the ordinate (*y*-axis) for 29.4 mL on the abscissa (*x*-axis) is - 0.03 mL (to the nearest 0.01 mL).

Burette reading: 29.43 mL, Correction: − 0.03 mL
Actual volume = 29.43 − 0.03 = 29.40 mL

Ways to detect systematic error:

1. Analyze samples of known composition, such as a Standard Reference Material.Your method should reproduce the known answer.

2. Analyze "blank" samples containing none of the analyte being sought. If you observe a nonzero result, your method responds to more than you intend. Section 29-3 discusses different kinds of blanks.

3. Use different analytical methods to measure the same quantity. If the results do not agree, there is error in one (or more) of the methods.

4. *Round robin* experiment: Assign different people in several laboratories to analyze identical samples by the same or different methods. Disagreement beyond the estimated random error is systematic error.

2) **Random error**, also called **indeterminate error**, arises from the effects of uncontrolled (and may be uncontrollable) variables in the measurement. Random error has an equal chance of being positive or negative. It is always present and cannot be corrected.

   Examples:
   1) Errors associated with reading a scale.

      - pH meter
      - Absorbance or percent transmittance

– volume delivered from a burette

2) Error results from random electrical noise in an instrument.

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***Random error* cannot be eliminated, but it might be reduced by a better experiment.**

Precision and Accuracy

Precision describes the reproducibility of a result. If you measure a quantity several times and the values agree closely with one another, your measurement is precise.

Accuracy describes how close a measured value is to the “true” value. If a known standard is available such as a Standard Reference Material, accuracy is how close your value is to the known value.

Absolute and Relative Uncertainty

Absolute uncertainty expresses the margin of uncertainty associated with a measurement. If the estimated uncertainty in reading a calibrated burette is ± 0.02 mL, we say that ± 0.02 mL is the absolute uncertainty associated with the reading.

An uncertainty of ± 0.02 means that, when the reading is 13.33, the true value could be anywhere in the range 13.31 to 13.35.

Relative uncertainty compares the size of the absolute uncertainty with the size of its associated measurement.

Example:
A buret reading = 24.45 ± 0.02 mL
Absolute uncertainty = ± 0.02

$$Relative\ Uncertainty = \frac{absolute\ uncertainty}{magnitude\ of\ measurement}$$

$$= \frac{0.02\ mL}{24.45\ L} = 0.0008$$

$$Percent\ relative\ uncertainty = relative\ uncertainty\ \times 100$$

= 0.0008 × 100 = 0.08%

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volume	Absolute uncertainty	% relative uncertainty
10 mL	± 0.02	0.2%
20 mL	± 0.02	0.1%
40 mL	± 0.02	0.05%

If you use a 50-mL burette, design your titration to require 20–40 mL of reagent to produce a small relative uncertainty of 0.1–0.05%.

- 20 mg/L is equal to…………g/m^3
- 20 mg/L is equal to ……………ppm

- Determine the number of significant digits in the following numbers
  - 142.7 — 142.70
  - 0.000006302 — 9.25×10^4
  - 9.250×10^4 — 9.2500×10^4
  - 0.3050 — 0.003050
  - 1.003×10^4

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Express the answer of each of the following with the correct # of Significant Figures

- Addition and Subtraction
  - $1.362 \times 10^4 + 3.111 \times 10^4 =$
  - $5.345 + 6.728 =$
  - $7.26 \times 10^{14} – 6.69 \times 10^{14} =$
  - $1.632 \times 10^5 + 4.107 \times 10^3 + 0.984 \times 10^6 =$
  - $3.021 + 8.99 =$
  - $12.7 – 1.83 =$

- Multiplication and Division
  - $3.26 \times 10^{-5} \times 1.78 =$
  - $4.3179 \times 10^{12} \times 3.6 \times 10^{-19} =$
  - $34.60 \div 2.46287 =$
  - $0.0302 \div (2.1143 \times 10^{-3}) =$
  - $6.345 \times 2.2 =$

- Logarithms and Antilogarithms
  - log 339 = — log 1237 =
  - log (3.39×10^{-5}) = — log 3.2 =
  - antilog (-3.42) = — antilog 4.37 =
  - Log 0.001237 = — $10^{4.37} =$
  - $10^{-2.600} =$ — log (2.2×10^{-18}) =
  - antilog (-2.224) = — $10^{-4.555} =$