Chapter 3
Experimental Error

Every measurement has some uncertainty, which is called *experimental error*.

Uncertainty in Measurement

- A digit that must be estimated is called uncertain. A measurement always has some degree of uncertainty.

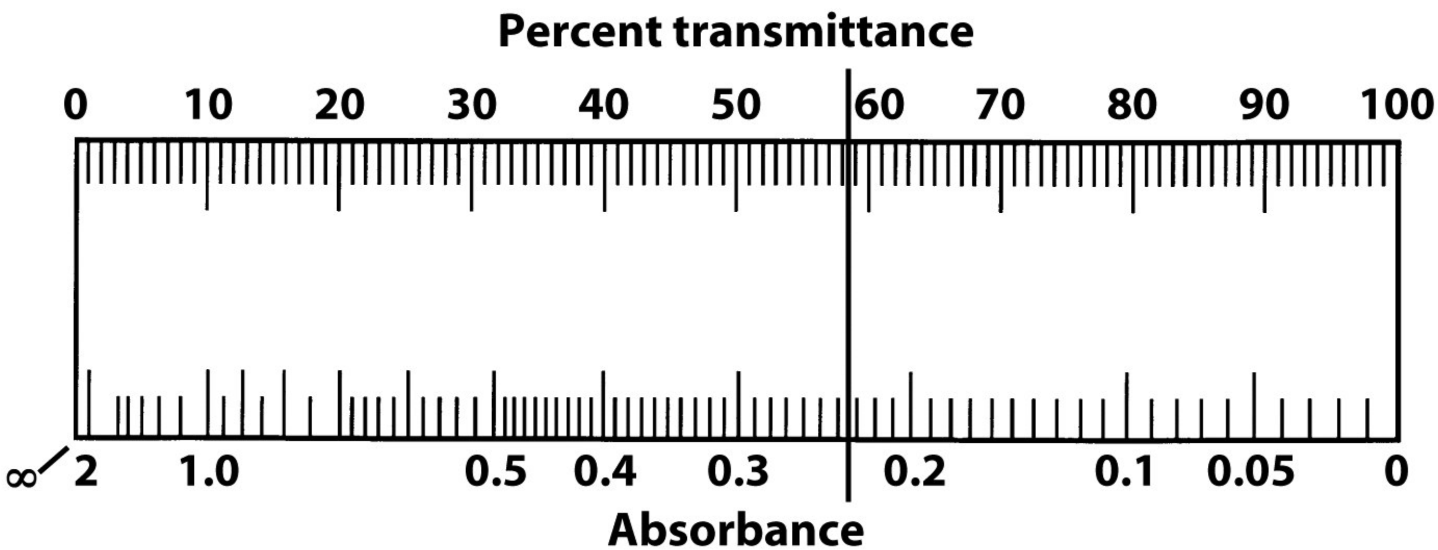
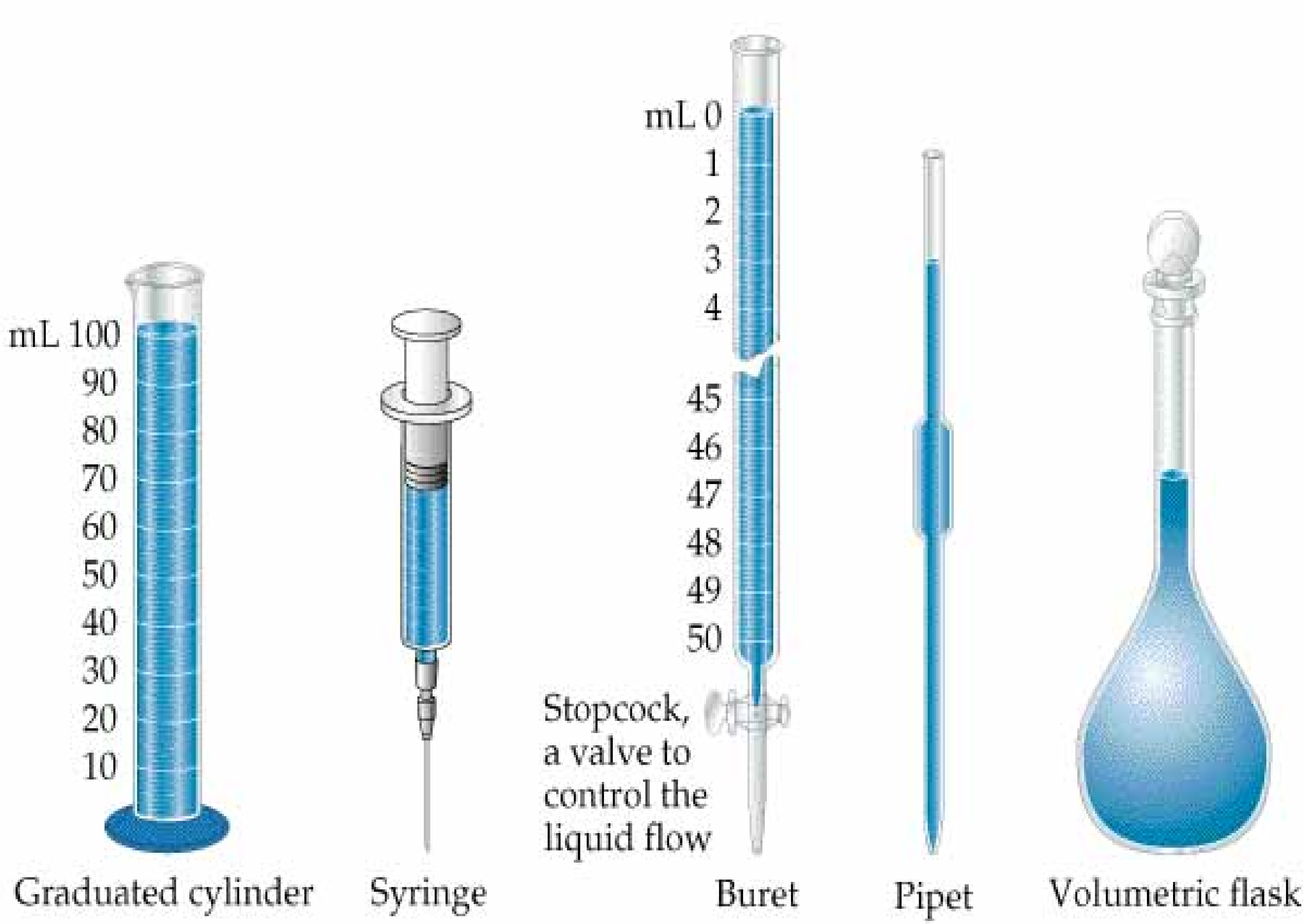
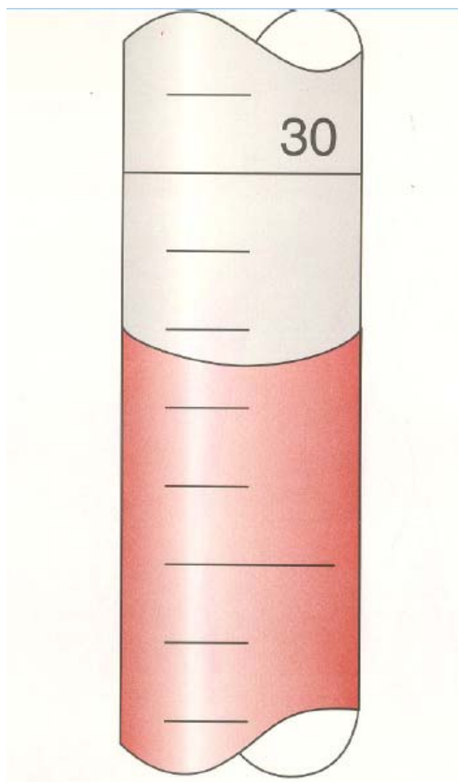


Figure 3-1
Quantitative Chemical Analysis, Seventh Edition


mL 100
90
80
70
60
50
40
30
20
10
mL 0
1
2
3
4
45
46
47
48
49
50
Stopcock, a valve to control the liquid flow
Graduated cylinder
Syringe
Buret
Pipet
Volumetric flask

Significant Figures

- 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.



30.2? mL

30.24 mL

30.25 mL

30.26 mL

Precision and Accuracy

- **Precision** - describes the **reproducibility** of measurements.
  - How close are results which have been obtained in exactly the same way?
  - The reproducibility is derived from the deviation from the **mean**.

- **Accuracy** - the closeness of the measurement to the **true or accepted value**.

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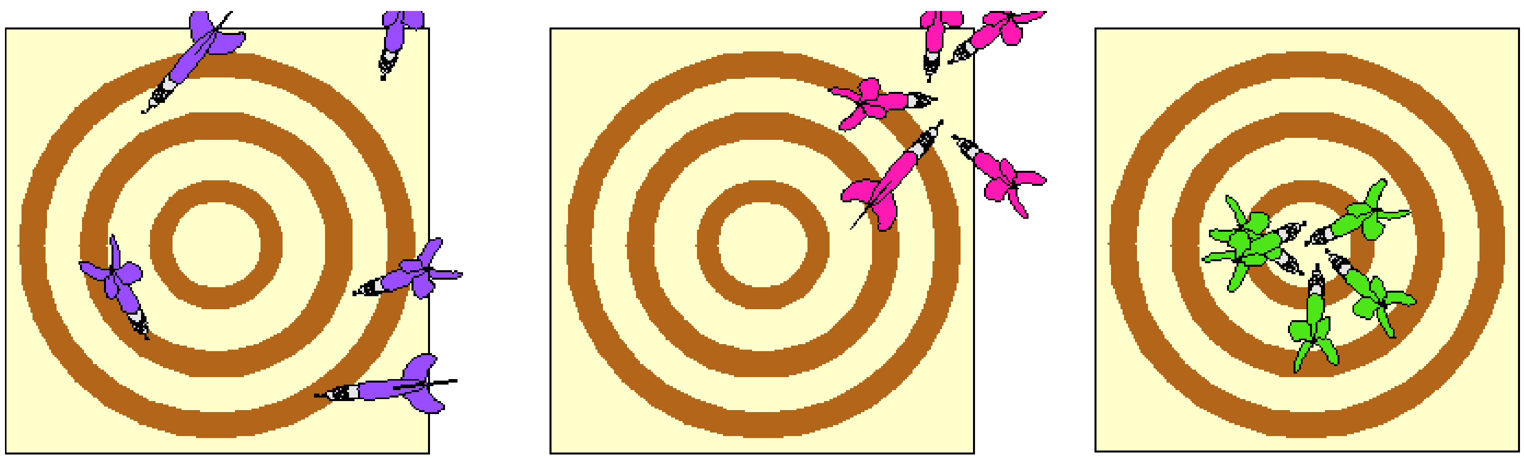
Precision and Accuracy

- **Accuracy** refers to the agreement of a particular value with the **“true”** value.

- **Precision** refers to the degree of agreement among several elements of the same quantity.



(a) (b) (c)

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Rules for Counting Significant Figures - Overview

- **Significant figures**: The minimum number of digits needed to write a given value in scientific notation without a loss of accuracy.
  - Nonzero integers
  - Zeros
    - leading zeros
    - captive zeros
    - Trailing zeros
  - Exact numbers

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Rules for Counting Significant Figures

- **Nonzero integers** always count as significant figures.

3456 has **4** significant figures.

Rules for Counting Significant Figures

- **Zeros**
  - **Leading zeros** do not count as significant figures.
  - **Leading zeros** simply indicate the position of the decimal point.
  - **0.0486** has **3** significant figures.

Rules for Counting Significant Figures

- **Zeros**
  - **Captive zeros** are located between nonzero digits.
  - **Captive zeros** always count as significant figures.

  - **16.07** has **4** significant figure.

Rules for Counting Significant Figures

- **Zeros**
  - **Trailing zeros are located at the right end of a number.**
  - **Trailing zeros** are significant only if the number contains a decimal point.
  - **9.300** has **4** significant figure.
  - When reporting 4600 ppb, use 4.6 ppm instead, assuming the two significant figures are reliable.

Significant Figures

- The number 92500 is ambiguous. It could mean any of the following:

9.25×10^4	3 significant figures
9.250×10^4	4 significant figures
9.2500×10^4	5 significant figures

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Significant Figures

- 144.8 — four significant figures
- 1.448×10^{2} — four significant figures
- $1.448\ 0 \times 10^{2}$ — five significant figures
- 6.302×10^{-6} — four significant figures
- 0.000 006 302 — four significant figures

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Significant Figures

- Significant zeros below are **bold**:

  1**0**6 0.01**0**6 0.1**0**6 0.1**0**6**0**

Rules for Counting Significant Figures - Details

- **Exact numbers** have an infinite number of significant figures.

1 inch = **2.54** cm, exactly

Rules for Significant Figures in Mathematical Operations

- **Addition and Subtraction:** decimal places in the result equals the number of decimal places in the least precise measurement.

6.8 + 11.934 = 18.734

$\rightarrow$ 18.7 (3 significant figure)

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Significant Figures in Addition and Subtraction

- **Addition/Subtraction:** The result should have the same number of decimal places as the least precise measurement used in the calculation.

1.784	3 decimal places
+ 0.91	2 decimal places

2.694	(too many decimal places; 4 is first insignificant figure)
2.69 proper answer	

15.62 + 12.5 + 20.4 = 48.52, the correct result is 48.5 because 12.5 has only one decimal place.

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Significant Figures
Addition/Subtraction

- In the addition or subtraction of numbers expressed in scientific notation, all numbers should first be expressed with the same exponent:

Example 2:

1.838×10^3 → 1.838×10^3 (both numbers with same exponent)

$+0.78 \times 10^4$ → $+7.8 \times 10^3$

9.638×10^3 (too many decimal places)

9.6 proper answer

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

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Rules for Significant Figures in Mathematical Operations

- **Multiplication and Division:** number of significant figures in the result equals the number in the least precise measurement used in the calculation.

$$6.38 \times 2.0 = 12.76$$

$\rightarrow$ 13 (2 significant figures)

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Significant Figures in Multiplication and Division

- **Multiplication/Division:** The number of significant figures in the result is the same as the number in the least precise measurement used in the calculation.

- It is common to carry one additional significant figure through extended calculations and to round off the final answer at the end.

8.9 g	Two significant figures
÷12.01 g/mol	Four significant figures

0.7411 mol	Too many significant figures
0.74 mol	proper answer (two significant figures)

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Significant Figures
Addition/Subtraction

- In multiplication and division, we are normally limited to the number of digits contained in the number with the fewest significant figures:
- The power of 10 has no influence on the number of figures that should be retained.

$$\begin{array}{rl} & 3.26 \times 10^{-5} \\ \times & 1.78 \\ \hline & 5.80 \times 10^{-5} \end{array}$$

$$\begin{array}{rll} & 4.317\,9 & \times 10^{12} \\ \times & 3.6 & \times 10^{-19} \\ \hline & 1.6 & \times 10^{-6} \end{array}$$

$$\begin{array}{rl} & 34.60 \\ \div & 2.462\,87 \\ \hline & 14.05 \end{array}$$

Rounding Data

- If the digit to be removed is less than 5, the preceding digit stays the same.

  For example, 2.33 is rounded to 2.3.

- If the digit to be removed is greater than 5, the preceding digit is increased by 1.

  For example, 2.36 is rounded to 2.4.

- If the digit to be removed is 5, round off the preceding digit to the nearest even number.

  Fore example, 2.15 becomes 2.2

  2.35 becomes 2.4.

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Significant Figures
Logarithms and Antilogarithms

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

Logarithm of n: $n = 10^a$ means that $\log n = a$

- The number *n* is said to be the **antilogarithm** of *a*.

- A logarithm is composed of a **characteristic** and a **mantissa**. The characteristic is the integer part and the mantissa is the decimal part:

$$\log 339 = \underbrace{2}_{\text{Characteristic} = 2}.\underbrace{530}_{\text{Mantissa} = 0.530} \qquad \log 3.39 \times 10^{-5} = \underbrace{-4}_{\text{Characteristic} = -4}.\underbrace{470}_{\text{Mantissa} = 0.470}$$

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Significant Figures
Logarithms and Antilogarithms

- Number of digits in ***mantissa*** of log ***x*** = number of significant figures in ***x***:

$$\log(\underbrace{5.403}_{\text{4 digits}} \times 10^{-8}) = -7.\underbrace{2674}_{\text{4 digits}}$$

- Number of digits in antilog ***x*** (= 10^x) = number of significant figures in ***mantissa*** of ***x***:

$$10^{6.\underbrace{142}_{\text{3 digits}}} = \underbrace{1.39}_{\text{3 digits}} \times 10^6$$

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Significant Figures
Logarithms and Antilogarithms

- 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*.

$$\log 0.001\,237 = -2.907\,6 \qquad \text{antilog } 4.37 = 2.3 \times 10^4$$
$$\log 1\,237 = 3.092\,4 \qquad 10^{4.37} = 2.3 \times 10^4$$
$$\log 3.2 = 0.51 \qquad 10^{-2.600} = 2.51 \times 10^{-3}$$

$$\log 0.001\,237 = -2.907\,6 \qquad \text{antilog } 4.37 = 2.3 \times 10^4$$
$$\log 1\,237 = 3.092\,4 \qquad 10^{4.37} = 2.3 \times 10^4$$
$$\log 3.2 = 0.51 \qquad 10^{-2.600} = 2.51 \times 10^{-3}$$

Exercises

3-1. How many significant figures are there in the following numbers?

(a) 1.903 0

(b) 0.039 10

(c) 1.40×10^4

(a) 5

(b) 4

(c) 3

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Exercises

3-2. Round each number as indicated:

(a) 1.236 7 to 4 significant figures

(b) 1.238 4 to 4 significant figures

(c) 0.135 2 to 3 significant figures

(d) 2.051 to 2 significant figures

(e) 2.005 0 to 3 significant figures

(a) 1.237 **(b)** 1.238 **(c)** 0.135 **(d)** 2.1 **(e)** 2.00

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Exercises

3-5. Write each answer with the correct number of digits.

(a) $1.021 + 2.69 = 3.711$

(b) $12.3 - 1.63 = 10.67$

(c) $4.34 \times 9.2 = 39.928$

(d) $0.060\,2 \div (2.113 \times 10^4) = 2.849\,03 \times 10^{-6}$

(e) $\log(4.218 \times 10^{12}) = ?$

(f) $\text{antilog}(-3.22) = ?$

(g) $10^{2.384} = ?$

(a) 3.71 **(b)** 10.7 **(c)** 4.0×10^1 **(d)** 2.85×10^{-6} **(e)** 12.625
(f) 6.0×10^{-4} **(g)** 242

Exercises

3-7. Write each answer with the correct number of significant figures.

(a) $1.0 + 2.1 + 3.4 + 5.8 = 12.300\ 0$

(b) $106.9 - 31.4 = 75.500\ 0$

(c) $107.868 - (2.113 \times 10^{2}) + (5.623 \times 10^{3}) = 5\ 519.568$

(d) $(26.14/37.62) \times 4.38 = 3.043\ 413$

(e) $(26.14/(37.62 \times 10^{8})) \times (4.38 \times 10^{-2}) = 3.043\ 413 \times 10^{-10}$

(f) $(26.14/3.38) + 4.2 = 11.933\ 7$

(g) $\log(3.98 \times 10^{4}) = 4.599\ 9$

(h) $10^{-6.31} = 4.897\ 79 \times 10^{-7}$

(a) 12.3 **(b)** 75.5 **(c)** 5.520×10^{3} **(d)** 3.04 **(e)** 3.04×10^{-10} **(f)** 11.9 **(g)** 4.600 **(h)** 4.9×10^{-7}

Experimental Error

- Data of unknown quality are useless!
- All laboratory measurements contain experimental error.
- It is necessary to determine the magnitude of the accuracy and reliability in your measurements.
- Then you can make a judgment about their usefulness.

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Precision and Accuracy

- **Precision** - describes the **reproducibility** of measurements.
  - How close are results which have been obtained in exactly the same way?
  - The reproducibility is derived from the deviation from the **mean**.

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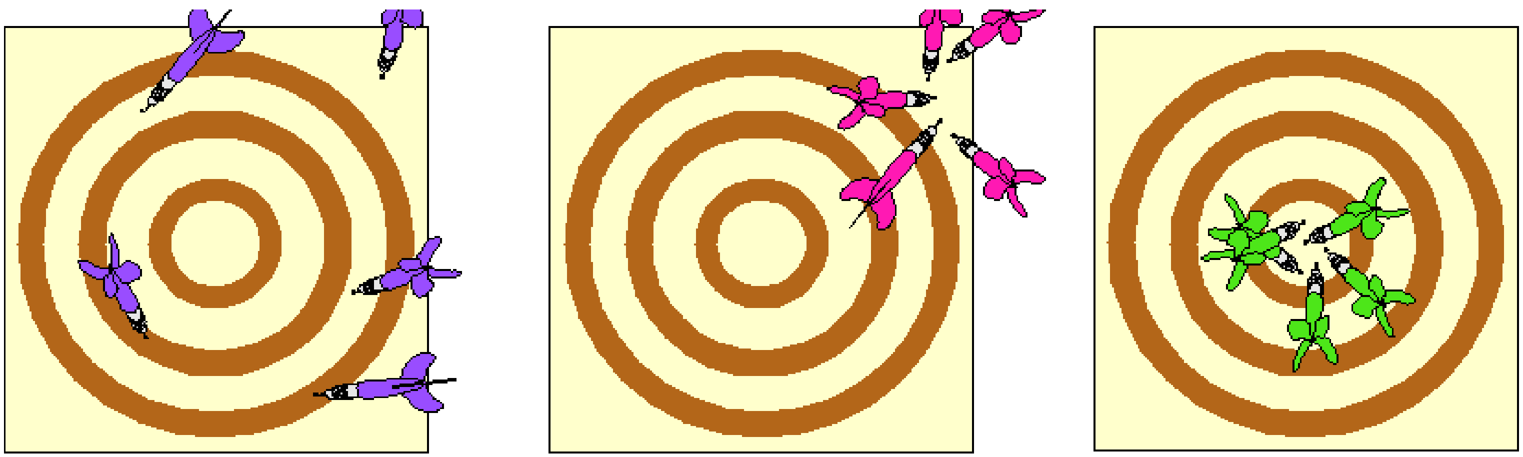
- **Precision** refers to the degree of agreement among several elements of the same quantity.



(a) (b) (c)

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Experimental Error

- **Replicates** - two or more determinations on the same sample.

One student measured Fe (III) concentrations six times.

The results were listed below:

19.7, 19.5, 19.4, 19.6, 20.2, 20.0 ppm (parts per million)

6 replicates = **6 measurements**

- **Mean:** average or arithmetic mean

$$\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N}$$

- **Median:** the middle value of replicate data
  - If an odd number of replicates, the middle value of replicate data.
  - If an even number of replicates, the middle two values are averaged to obtain the median.

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Systematic Error

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

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Random Error

- **Random error** (or **indeterminate error**) arises from the effects of uncontrolled variables in the measurement.

- Random error has an equal chance of being positive or negative.

- It is always present and cannot be corrected.

Absolute and Relative Uncertainty

- **Absolute uncertainty** expresses the margin of uncertainty associated with a measurement.
- **Relative uncertainty** compares the size of the absolute uncertainty with the size of its associated measurement.

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

$$\text{Percent relative uncertainty} = 100 \times \text{relative uncertainty}$$

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Propagation of Uncertainty from Random Error

Table 3-1 Summary of rules for propagation of uncertainty

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

a. x represents a variable and a represents a constant that has no uncertainty.

b. e_x/x is the relative error in x and $\%e_x$ is $100 \times e_x/x$.

Propagation of Uncertainty from Random Error

- **Uncertainty in Addition and Subtraction**

$$
\begin{array}{rl}
 & 1.76\ (\pm 0.03) \leftarrow e_1 \\
+ & 1.89\ (\pm 0.02) \leftarrow e_2 \\
- & 0.59\ (\pm 0.02) \leftarrow e_3 \\
\hline
 & 3.06\ (\pm e_4)
\end{array}
$$

$$e_4 = \sqrt{e_1^2 + e_2^2 + e_3^2}$$

$$e_4 = \sqrt{(0.03)^2 + (0.02)^2 + (0.02)^2} = 0.04_1$$

$$\text{Percent relative uncertainty} = \frac{0.04_1}{3.06} \times 100 = 1._3\%$$

3.06 (±0.04) (absolute uncertainty)

3.06 (±1%) (relative uncertainty)

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Propagation of Uncertainty from Random Error

- **Uncertainty in Addition and Subtraction**
- Always retain more digits than necessary during a calculation and round off to the appropriate number of digits at the end.

$$\begin{array}{r} 17.88\ (\pm 0.02) \\ -\ 0.05\ (\pm 0.02) \\ \hline 17.83\ (\pm e) \end{array}$$

$$e = \sqrt{0.02^2 + 0.02^2} = 0.02_8 \approx 0.03$$

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Propagation of Uncertainty from Random Error

- **Uncertainty in** Multiplication and Division

$$\%e_4 = \sqrt{(\%e_1)^2 + (\%e_2)^2 + (\%e_3)^2}$$

$$\frac{1.76\ (\pm 0.03) \times 1.89\ (\pm 0.02)}{0.59\ (\pm 0.02)} = 5.64 \pm e_4$$

- First convert absolute uncertainties into percent relative uncertainties.

$$\frac{1.76\ (\pm 1._7\%) \times 1.89\ (\pm 1._1\%)}{0.59\ (\pm 3._4\%)} = 5.64 \pm e_4$$

$$\%e_4 = \sqrt{(1._7)^2 + (1._1)^2 + (3._4)^2} = 4._0\%$$

- To convert relative uncertainty into absolute uncertainty

$$4._0\% \times 5.6_4 = 0.04_0 \times 5.6_4 = 0.2_3$$

$$5.6\ (\pm 0.2) \qquad \text{(absolute uncertainty)}$$

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Exercises

- 3-A (a) Find the absolute and percent relative uncertainty for each answer.

[12.41 (±0.09) ÷ 4.16 (±0.01)] × 7.068 2 (±0.0004) = ?

$$\frac{12.41\ (\pm 0.725\%) \times 7.068\ 2\ (\pm 0.0057\%)}{4.16\ (\pm 0.240\%)}$$

$$\sqrt{0.725^2 + 0.0057^2 + 0.240^2} = 0.764$$

$$= 21.086\ (\pm 0.764\%)$$

$$= 21.0_9\ (\pm 0.1_6) = 21.1\ (\pm 0.2)$$

$$\text{relative uncertainty} = \frac{0.1_6}{21.0_9} \times 100 = 0.8\%$$

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Propagation of Uncertainty from Random Error

- **The Real Rule for Significant Figures**
  - *The first digit of the absolute uncertainty is the last significant digit in the answer*.

$$\frac{0.002\,364\,(\pm 0.000\,003)}{0.025\,00(\pm 0.000\,05)} = 0.094\,6\,(\pm 0.000\,2)$$

- The uncertainty (±0.000 2) occurs in the fourth decimal place.
- The answer 0.094 6 is properly expressed with *three* significant figures, even though the original data have four figures.
- The first uncertain figure of the answer is the last significant figure.

Propagation of Uncertainty from Random Error

- **The Real Rule for Significant Figures**
  - *The first digit of the absolute uncertainty is the last significant digit in the answer*.

$$\frac{0.821\ (\pm 0.002)}{0.803\ (\pm 0.002)} = 1.022\ (\pm 0.004)$$

The quotient is expressed with *four* figures even though the dividend and divisor each have *three* figures.

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Propagation of Uncertainty from Random Error

- **Mixed Operations**

$$\frac{[1.76\ (\pm 0.03) - 0.59\ (\pm 0.02)]}{1.89\ (\pm 0.02)} = 0.619_0 \pm ?$$

- First work out the difference in the numerator. $\sqrt{(0.03)^2 + (0.02)^2} = 0.03_6.$

$$1.76\ (\pm 0.03) - 0.59\ (\pm 0.02) = 1.17\ (\pm 0.03_6)$$

- Then convert into percent relative uncertainties

$$\frac{1.17\ (\pm 0.03_6)}{1.89\ (\pm 0.02)} = \frac{1.17\ (\pm 3._1\%)}{1.89\ (\pm 1._1\%)} = 0.619_0\ (\pm 3._3\%)$$

$$\sqrt{(3._1\%)^2 + (1._1\%)^2} = 3._3\%$$

$0.62\ (\pm 0.02)$ (absolute uncertainty)

$0.62\ (\pm 3\%)$ (relative uncertainty)

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Exercises

- 3-A (b) Find the absolute and percent relative uncertainty for each answer.

$[3.26\ (\pm0.10) \times 8.47\ (\pm0.05)] - 0.18\ (\pm0.06) = ?$

$= [3.26\ (\pm3.07\%) \times 8.47\ (\pm0.59\%)] - 0.18\ (\pm0.06)$

$= [27.612\ (\pm3.13\%)] - 0.18\ (\pm0.06)$

$= [27.612\ (\pm0.864)] - 0.18\ (\pm0.06)$

$= 27.4\ (\pm0.9)$

Relative uncertainty = 3%

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Propagation of Uncertainty from Random Error

- Exponents and Logarithms

Function[a]	Uncertainty[b]
$y = x^a$	$\%e_y = a\%e_x$
$y = \log x$	$e_y = \frac{1}{\ln 10}\frac{e_x}{x} \approx 0.434\,29\frac{e_x}{x}$
$y = \ln x$	$e_y = \frac{e_x}{x}$
$y = 10^x$	$\frac{e_y}{y} = (\ln 10)e_x \approx 2.302\,6\,e_x$
$y = e^x$	$\frac{e_y}{y} = e_x$

Exercises

- 3-A (b) Find the absolute and percent relative uncertainty for each answer.

$$\sqrt{3.24 \pm 0.08} = ?$$

$$\%e_y = a\%e_x$$

$$= 1.80 \pm 1.235\%$$

$$\tfrac{1}{2}\left(\frac{0.08}{3.24} \times 100\right) = 1.235\%$$

$$= 1.80 \pm 0.02$$

Exercises

(f) $\log(3.24 \pm 0.08) = ?$

(f) $e_y = 0.434\,29 \dfrac{e_x}{x} = 0.434\,29 \left(\dfrac{0.08}{3.24}\right) = 0.010\,7$

$\log(3.24 \pm 0.08) = 0.510\,5 \pm 0.010\,7$

$= 0.51 \pm 0.01\ (\pm 2_{.1}\%)$

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Exercises

(e) $(3.24 \pm 0.08)^4 = ?$

(e) $\%e_y = 4\%e_x = 4\left(\dfrac{0.08}{3.24} \times 100\right) = 9.877\%$

$(3.24 \pm 0.08)^4 = 110.20 \pm 9.877\%$

$= 1.1_0\ (\pm 0.1_1) \times 10^2 (\pm 9._9\%)$

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Propagation of Uncertainty from Random Error

- Consider the function pH = −log [H^+], where [H^+] is the molarity of H^+. For pH = 5.21 ± 0.03, find [H^+] and its uncertainty.

$$[H^+] = 10^{-pH} = 10^{-(5.21 \pm 0.03)}$$

$$\frac{e_y}{y} = 2.302\,6\, e_x = (2.302\,6)(0.03) = 0.069\,1$$

$$y = 10^{-5.21} = 6.17 \times 10^{-6}$$

$$\frac{e_y}{y} = \frac{e_y}{6.17 \times 10^{-6}} = 0.069\,1 \quad \Rightarrow \quad e_y = 4.26 \times 10^{-7}$$

- The concentration of H^+ is 6.17 (±0.426) × 10^{-6} = 6.2 (±0.4) × 10^{-6} M.

Summary

- The number of significant digits in a number is the **minimum** required to write the number in scientific notation.
- The **first** uncertain digit is the **last** significant figure.
- In **addition and subtraction**, the last significant figure is determined by the number with the fewest decimal places (when all exponents are equal).
- In **multiplication and division**, the number of figures is usually limited by the factor with the smallest number of digits.
- The number of figures in the **mantissa** of the logarithm of a quantity should equal the number of significant figures in the quantity.
- **Random** (indeterminate) error affects the precision (reproducibility) of a result, whereas **systematic** (determinate) error affects the accuracy (nearness to the "true" value).

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Summary

- **Systematic** error can be discovered and eliminated by a clever person, but some **random** error is always present.

- For random errors, propagation of uncertainty in addition and subtraction requires **absolute** uncertainties whereas multiplication and division utilize **relative** uncertainties.

- Other rules for propagation of random error are found in Table 3-1.

- Always retain more digits than necessary during a calculation and round off to the appropriate number of digits at the end.

- **Systematic** error in atomic mass or the volume of a pipet leads to larger uncertainty than we get from **random** error. We always strive to eliminate systematic errors.

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