

## Experimental Error: What is the "truth"?

We don't (and can't) determine the "true value" of any component in a mixture.

- All measurements have some associated error (*uncertainty*).

We can work to understand (and improve) the *precision* of a measurement.

**Precision =**

Comparing multiple methods increases confidence in the *accuracy* of our results.

**Accuracy =**

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## Representation of Analytical Data

**Significant Figures:** Minimum number of digits required to express a value in scientific notation without a loss of precision.

*Last digit has uncertainty, at least  $\pm 1$ !*

Ideally results are presented to the appropriate number of significant figures, and accompanied by the error in the final digit.

Value  $\pm$  Error

e.g.  $102.5 \pm 0.1$  ppm

When rounding, look at all digits beyond the last place needed.

Always round values that are exactly halfway to the nearest **even** digit.

12.250  $\rightarrow$  12.2

12.350  $\rightarrow$  12.4

12.250001  $\rightarrow$  12.3

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## Guidelines for Sig. Figs

1. all nonzero digits are significant,
2. all zeros that appear between nonzero digits of a number are significant,
3. all zeros at the end of a number on the right hand side of the decimal point are significant,
4. all other zeros are not significant.

### Examples:

Value	# Significant Figures
14600	
0.0146	
1406	
0.010460	

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## Sig Figs in Calculations

In doing calculations, the number significant figures is limited by the least certain piece of data.

### Addition/Subtraction

### Multiplication/Division

### Example:

How many sig. figs. should be in the answers to the following:

$$126.23 + 0.0147 =$$

$$58.6 \times 3.1 =$$

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## Sig Figs in Calculations

**Logarithms:** if  $n = 10^a$ , then  $\log n = a$

The number of sig. figs. in **a** should be the same as the number of sig. figs. in **n**.

**BUT**, the only significant figures in **a** are in the mantissa (after the decimal point).

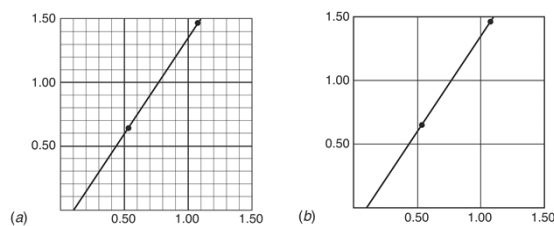
**Example:** What is the log of 3250? 0.01370?

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## Sig Figs in Calculations

**Graphing:**

- If someone is going to need to extract data from your graph, it must be set up to allow the appropriate accuracy (# sig. figs) to be read as well.



**Experimentally-Determined Values:**

**The real rule for sig. figs.:** The first digit that has some associated uncertainty is the last significant digit.

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## Types of Error

### Systematic Error:

Detecting Systematic Error...How?

### Random Error

### Absolute Uncertainty

### Relative Uncertainty, Percent Relative Uncertainty

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## Error Propagation

*How do errors (uncertainties) in individual values affect an analysis?*

- Effects depend on how the data is used.

Overall uncertainty is often dominated by one component

- The “weakest link”
- If we understand the contribution of each component to uncertainty, we can predict what “reasonable” precision is for a measurement.

What matters? Can we estimate uncertainty?

See [http://chemwiki.ucdavis.edu/Analytical\\_Chemistry/Quantifying\\_Nature/Significant\\_Digits/Propagation\\_of\\_Error](http://chemwiki.ucdavis.edu/Analytical_Chemistry/Quantifying_Nature/Significant_Digits/Propagation_of_Error) for a more extensive discussion of the underlying calculus.

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## Error Propagation

### Error Propagation in Addition and Subtraction:

- Overall error is based on the absolute uncertainties of individual values.

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

- Example:

$$\begin{array}{r} 12.4 \pm 0.2 \\ 5.7 \pm 0.1 \\ + 1.43 \pm 0.04 \\ \hline 19.53 \pm ??? \end{array}$$

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## Error Propagation

### Error Propagation in Multiplication and Division

- Concept is the same as addition and subtraction, except *relative uncertainties* are used

$$\left(\frac{e_D}{D}\right)^2 = \left(\frac{e_A}{A}\right)^2 + \left(\frac{e_B}{B}\right)^2 + \left(\frac{e_C}{C}\right)^2 \quad \text{or} \quad \%e_D = \sqrt{(\%e_A)^2 + (\%e_B)^2 + (\%e_C)^2}$$

- Let's say we have a product to consider, how do we determine the relative and absolute uncertainty in C ( $e_C$ )?

$$(A \pm e_A) \times (B \pm e_B) = C \pm e_C$$

$$\frac{e_C}{C} = \sqrt{\left(\frac{e_A}{A}\right)^2 + \left(\frac{e_B}{B}\right)^2}$$

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## Error Propagation

**Example:** You are titrating a solution of sulfuric acid of unknown concentration with a standardized  $0.106 \pm 0.002$  M sodium hydroxide solution. In titrating  $25.00 \pm 0.03$  mL of the  $\text{H}_2\text{SO}_4$ , your initial buret reading is  $1.25 \pm 0.05$  mL and the reading at the endpoint is  $33.84 \pm 0.05$  mL. What is the sulfuric acid concentration and its associated absolute uncertainty?

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## Error Propagation

Logs, exponents, powers, etc. have varying rules (Table 3-1). You should know how to use the rules if you are given this table.

**TABLE 3-1** Summary of rules for propagation of uncertainty

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

*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  $100 \times e_x/x$ .

Harris, *Quantitative Chemical Analysis*, 8e

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