

# Treatment of Experimental Data

## I. PRECISION AND ACCURACY

The only kind of physical quantity that can be measured with perfect accuracy is a tally of discrete objects, for example, dollars and cents or the number of objects in a museum case. In measuring a quantity capable of continuous variation such as mass or length there always is some uncertainty because the answer, like an irrational number such as  $\pi$ , cannot be expressed by any finite number of digits. The volume of liquid in a buret, for example, is capable of continuous variation and can only be estimated because obtaining a measurement requires guessing just where the liquid level lies between marked volume divisions on the buret wall. The precision of the volume estimate depends on the quality of the buret and the skill of the experimenter. In addition to errors which result from difficulties of constructing and using measuring devices, other errors over which the experimenter has no control are inherent in measurements. Therefore, at least two, preferably three or more, determinations of any quantity should be made for comparison purposes. After making several measurements of some quantity, the best value to use generally is the average of all the measurements. The "true" value—more correctly, the "accepted" value—of important quantities such as physical constants listed in a handbook (for example, the velocity of light in a vacuum), is chosen by some competent group of experts who critically examine all the available data to select the most probable value.

It is important to distinguish between the **precision** and the **accuracy** of a series of measurements.

**The precision indicates how reproducible the measurements are.**

Measurements whose values scatter widely are less precise than measurements whose values lie close together, even though the average value of the two sets of data might be exactly the same. Measurements of the diameter of a solid cylinder made with a micrometer will be more precise than the same measurements made with a meter stick because the meter stick is more coarsely graduated.

**The accuracy indicates how well the measurement agrees with an accepted value.**

The accuracy of a measurement is unrelated to its precision. Accuracy depends on how well the measuring device is calibrated with respect to some accepted standard, such as the international reference meter length at the National Bureau of Standards. If a precise micrometer reads 1.50 mm when it actually should measure 1.75 mm, then the average value of a very precise series of measurements will be in error by 0.25 mm, inaccurate by:  $(0.25/1.75)(100\%) = 14.3\%$ .

One can only judge the accuracy of a measurement by comparing it with an accepted value. If no accepted value can be found, the accuracy cannot be ascertained.

## II. DETERMINING PRECISION:

The precision of an experimental determination may be taken to be a statement about how widely the individual values of a series of measurements deviate from the average value. The arithmetic average of a series of measurements is usually taken to be the "best" value, but the average value gives no information about the precision, or "scatter", of the separate measurements. The most common ways to express experimental precision are by the **average deviation**, **relative average deviation**, and **standard deviation**.

### 1. Average Deviation

The simplest measure of precision is the **average deviation**, which is determined as follows:

1. Calculate the average value of all the of measurements
2. Subtract the average value from each individually measured value; this quantity is called the **deviation**,
3. Sum the deviations (treat each deviation, whether positive or negative, as a positive quantity) and calculate their average.

Written as an equation, the average deviation  $\bar{d}$  is:

$$\bar{d} = \frac{\sum_{i=1}^n |x_i - \bar{x}|}{n}$$

where  $n$  is the total number of measurements, the summation goes from  $i=1$  (the value of  $x$  for the first measurement) to  $i=n$  (the value of  $x$  for the  $n$ th measurement),  $x_i$  is the value of the  $i$ th measurement, and  $\bar{x}$  is the average value of all the measurements. The vertical lines on each side of the parenthesis in the numerator are an **absolute value** symbol. They indicate that the quantity between them is to be regarded as a positive quantity.

**Using the absolute value of a number simply means always treating the number as a positive quantity, regardless of whether the true value is positive or negative.**

The numerator, then, is the sum of the absolute values of all the deviations.

#### EXAMPLE 1:

In a series of measurements, the following values for the molarity of a potassium permanganate solution were obtained: 0.1010, 0.1020, 0.1012, 0.1015 mol L<sup>-1</sup> (moles per liter). Calculate the average deviation.

#### ANSWER:

Individual measurements	Individual deviations from the average (absolute value)
0.1010	0.1014 - 0.1010 = 0.0004
0.1020	0.1014 - 0.1020 = 0.0006
0.1012	0.1014 - 0.1012 = 0.0002
<u>0.1015</u>	0.1014 - 0.1015 = 0.0001
$\Sigma x_i = 0.4057$	$\Sigma d_i = 0.0013$

$$\text{Average } x = \bar{x} = \frac{0.4057}{4} = 0.1014 \text{ mol/L}$$

$$\text{Average deviation} = \bar{d} = \frac{0.0013}{4} = 0.0003 \text{ mol/L}$$

These results would be reported as: **0.1014 ± 0.0003 mol/L.**

## 2. Relative Average Deviation

Precision also may be expressed as the **relative average deviation (r.a.d.)**, defined as *the average deviation divided by the average value.*

#### EXAMPLE 2:

The r.a.d. for the measurements in Example 1 is:

$$\text{r.a.d.} = \frac{\text{av. deviation}}{\text{av. measured value}} = \frac{\bar{d}}{\bar{x}} = \frac{0.0003}{0.1014} = 0.003 \text{ (dimensionless)}$$

(Only one significant figure is valid.) The percent r.a.d. is an often used variation. It is obtained by multiplying the r.a.d. by 100%:

$$\text{r.a.d.} = \frac{0.0003}{0.1014} \times 100\% = 0.3\%$$

The precision of an experiment varies with the method and apparatus used. An experienced chemist using equipment commonly available for routine analytical work should be able to determine the chloride concentration in a solution with a precision of 0.1% r.a.d. The average inexperienced student is more likely to obtain a precision around 1.0% r.a.d.

## 3. Standard Deviation

The **standard deviation** has greater theoretical validity than the average deviation. The average deviation is popular because of its simplicity but is reliable only if the number of measurements is very large, around 10 or more. For smaller sets of data, the standard deviation gives a much better indication of

measuring precision. Both methods indicate the same precision for random errors in a very large number of measurements.

The standard deviation is determined as follows:

1. Calculate the average of a series of measurements.
2. Determine the deviation of each measurement from the average.
3. Square the deviations and add up their squares.
4. Divide the sum of the squares of the deviations by  $(n - 1)$ , where  $n$  is the total number of measurements.
5. Take the square root of the result from step 4.

Let  $x_1$  be the value of the first measurement,  $x_2$  the value of the second, and so forth. Let  $\bar{x}$  be the average value of all the measurements. Then the deviations in step 2 above are found as in the average deviation, by subtracting the average value from each measured value. Let the deviation of measurement 1 be  $d_1$ , of measurement 2 be  $d_2$ , etc. Then:

$$\begin{aligned}d_1 &= x_1 - \bar{x} \\d_2 &= x_2 - \bar{x} \\d_3 &= x_3 - \bar{x} \\&\text{etc.}\end{aligned}$$

Written as an equation, the standard deviation  $\sigma$  is:

$$\sigma = \left( \frac{d_1^2 + d_2^2 + d_3^2 + \dots + d_n^2}{n - 1} \right)^{1/2} = \left( \frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1} \right)^{1/2}$$

where  $n$  is the total number of measurements, the summation goes from  $i = 1$  (the value of  $x$  for the first measurement) to  $i = n$  (the value of  $x$  for the  $n$ th measurement),  $x_i$  is the value of the  $i$ th measurement, and  $\bar{x}$  is the average value of all the measurements. Example 3 illustrates how to determine the standard deviation of a series of measurements.

### EXAMPLE 3:

Calculate the standard deviation of the measurements in Example 1 of the molarity of a potassium permanganate solution.

### ANSWER:

Measurement number	Measured molarity (mol/L)	Individual deviations from the average	Deviations squared
1	0.1010	$0.1010 - 0.1014 = -0.0004$	$(-0.0004)^2 = 1.6 \times 10^{-7}$
2	0.1020	$0.1020 - 0.1014 = +0.0006$	$(+0.0006)^2 = 3.6 \times 10^{-7}$
3	0.1012	$0.1012 - 0.1014 = -0.0002$	$(-0.0002)^2 = 0.4 \times 10^{-7}$
4	<u>0.1015</u>	$0.1015 - 0.1014 = +0.0001$	$(+0.0001)^2 = 0.1 \times 10^{-7}$
	$\Sigma x_i = 0.4057$		$\Sigma d_i^2 = 6.6 \times 10^{-7}$

$$\text{Average molarity} = \frac{0.4057}{4} = 0.1014 \text{ mol/L} \quad \text{std. dev.} = \sigma = \left( \frac{6.6 \times 10^{-7}}{4 - 1} \right)^{1/2} = 0.00047 \text{ mol/L}$$

These results would be reported as:

**molarity of potassium permanganate solution =  $0.1014 \pm 0.0005$  mol/L (std. dev.).**

Notice that in this case, with only a few measurements, the standard deviation more realistically indicates less precision in the measurements than did the average deviation.

The standard deviation has a precise theoretical meaning.

**If the deviations from one measurement to another are perfectly random, the magnitude of the standard deviation gives the range of spread from the average value within which 68% of all repeated measurements are expected to fall.**

For example, if you make 100 duplicate measurements of the mass of a sample, 68 of these measurements should fall within plus or minus one standard deviation of the average value. Ninety-five percent of all duplicate measurements should lie within two standard deviations<sup>1</sup> ( $2\sigma$ : std. dev. multiplied by two). Two standard deviations ( $2s$ ) is said to represent the 95% confidence level. Testing these statements on an actual sample can be a useful way of determining whether or not the errors in a given measurement are truly random or not. If some systematic error is present, such as a steady drift in an instrument calibration due to a changing temperature, the precision predictions of the standard deviation will not hold true.

Like the average deviation, use of the standard deviation is strictly valid only for an infinite number of measurements. When the total number of replicate measurements is quite small, perhaps four or five, the standard deviation should be regarded only as a rough estimate, but it is better than the average deviation and is the most useful indication of measurement uncertainty for finite data sets.

### III. DETERMINING ACCURACY:

Precise measurements are not necessarily accurate. The **accuracy** expresses the agreement of the measurement with an accepted value for the quantity. If no accepted value is known, the accuracy cannot be ascertained. When a quantity is measured for which a "true" or accepted value is known, it is usual to express the accuracy in terms of the **absolute error** and **relative error**, both of which compare the measured value with the accepted value.

**The absolute error (also called just the error), is the experimentally determined value minus the accepted value.**

**The relative error is the absolute error divided by the accepted value.**

#### EXAMPLE 4:

Suppose that the accepted value for the normality of the permanganate solution in Example 1 is 0.1024 mol/L, as measured by the instructor of the course. What are the absolute error and relative error for the determination of the normality in Example 1?

#### ANSWER:

$$\begin{array}{ll} 0.1014 \text{ mol/L} & \text{the determined average value} \\ -0.1024 \text{ mol/L} & \text{the accepted value} \\ \hline -0.0010 \text{ mol/L} & \text{the absolute error} \end{array}$$

from which the relative error is  $-0.0098$ , obtained as follows:

$$\frac{-0.0010}{0.1024} = -0.0098$$

Notice that there are no units for the relative error.

Other ways to express relative error are by **percent relative error (%)**, **parts per thousand (ppt)**, and **parts per million (ppm)**. The relative error from above may also be expressed as:

$$\begin{array}{ll} -0.0098 \times 100\% & = -0.98\% \\ -0.0098 \times 1000 \text{ ppt} & = -9.8 \text{ ppt} \\ -0.0098 \times 1,000,000 \text{ ppm} & = -9800 \text{ ppm} \end{array}$$

### IV. PROPAGATION OF ERRORS:

Often, several different measured quantities are used to calculate another quantity, as when the density of an object is found by dividing its measured mass by its measured volume. Uncertainties in the measured quantities naturally will result in an uncertainty in the calculated quantity. If the uncertainties in the measured quantities have been determined, the most probable, or **statistical uncertainty**, in a calculated quantity can be found by using the following rules.

<sup>1</sup> Actually, 95% of the measurements should lie within 1.96 standard deviations. Using a value of  $2\sigma$  is close enough and, in any case, it errs on the safe side.

### 1. Statistical uncertainty in sums and differences

Suppose a calculated quantity is  $F = x \pm y$ . Let  $U_F$ ,  $U_x$ , and  $U_y$  be the statistical uncertainties in  $F$ ,  $x$ , and  $y$ , respectively.

**The statistical uncertainty in  $F$  equals the square root of the sum of the squares of the uncertainties in  $x$  and  $y$ .**

In equation form:  $U_F = (U_x^2 + U_y^2)^{1/2}$ .

#### EXAMPLE 5:

The mass of water in a beaker is found by weighing the dry beaker empty and then weighing it with the water in it. The mass of the water is the difference between these two masses. Each mass is weighed four times. The results, with the calculated average deviations, are:

mass of beaker when empty ( $m_b$ ):	$9.8264 \pm 0.0005$ g
mass of beaker with water in it ( $m_{b+w}$ ):	$16.7193 \pm 0.0005$ g
mass of water (without uncertainties):	$m_w = m_{b+w} - m_b = 16.7193 - 9.8264 = 6.8929$ g
statistical uncertainty in mass of water:	$U_w = (0.0005^2 + 0.0005^2)^{1/2} = (5 \times 10^{-7})^{1/2}$ $U_w = \pm 0.0007$ g (rounded to one significant figure)

The measured mass of water is expressed correctly as:  $m_w = 6.8929 \pm 0.0007$  g

### 2. Statistical uncertainty in products and quotients

Suppose a calculated quantity is  $F = (xy)/z$ . Let  $U_F$ ,  $U_x$ , and  $U_y$  be the statistical uncertainties in  $F$ ,  $x$ , and  $y$ , respectively. The statistical uncertainty in  $F$  is:

$$U_F = F \left\{ \left( \frac{U_x}{x} \right)^2 + \left( \frac{U_y}{y} \right)^2 + \left( \frac{U_z}{z} \right)^2 \right\}^{1/2}$$

#### EXAMPLE 6:

The density of an object is found by dividing its measured mass by its measured volume. The volume and mass each are measured seven times, the mass on an analytical balance and the volume by displacing water in a graduated cylinder. The results, with their calculated standard deviations, are:

mass of object:	$m = 9.2152 \pm 0.0003$ g
volume of object:	$V = 8.74 \pm 0.07$ mL
density of object (without uncertainties):	$r = 9.2152/8.74 = 1.05$ g/mL

statistical uncertainty in density:  $U_d = (1.05) \left\{ \left( \frac{0.0003}{9.2152} \right)^2 + \left( \frac{0.07}{8.74} \right)^2 \right\}^{1/2} = \pm 0.008$  g/mL

The measured density is correctly expressed as:  $r = 1.05 \pm 0.01$  g/mL (rounded to 2 decimal places)

This example illustrates a very important point.

**The precision of a result calculated by multiplication and/or division can be no greater than the precision of the least precise quantity used in the calculation.**

When different measurements are combined in a calculation to obtain a new quantity, such as dividing mass by volume to get density, the precisions of the different measurements will, in general, be different. It can be seen that the uncertainty in the density measurement is dominated by the uncertainty of the volume measurement, which is known only to three significant figures. A less precise balance could have been used without decreasing the precision of the measurement at all. If a more precise density measurement is needed, the precision of the volume measurement must be improved first. There is no point in improving the mass measurement alone because it would make no difference in the final uncertainty of the density value.

## V. SIGNIFICANT FIGURES:

Whenever a measured value is given, the number should be expressed in a manner that makes the degree of uncertainty perfectly clear. This is done by writing a value so that it contains only those digits that are known with certainty (have not been estimated), plus one more figure (the first estimated figure). The last figure in the number is always one that requires some degree of estimation and, therefore, it serves as an indication of the precision of the value.

**Significant figures are the number of digits necessary to express a measurement or calculation to the precision with which it was made.**

It is important to remember that the number of significant figures is unrelated to the position of the decimal point. The numbers 1056, 105.6, 1.056, 0.1056, 0.001056, and  $1.056 \times 10^7$  all are written with just four significant figures. Zeroes which serve only to locate the decimal point, as the first two zeroes in 0.001056, and powers of ten which are needed to express the magnitude of a value, do not count as significant figures.

Usually, there is no problem in reporting the correct number of significant figures to express the result of a direct measurement because the measuring instrument simply does not give extra meaningless figures. However, when calculations are performed to obtain some desired quantity, extra numbers often appear that have no experimental validity. This is especially true when using an electronic calculator. Extra meaningless figures always should be eliminated by rounding off the calculated value to the correct number of significant figures.

### Rules for Rounding Off to the Correct Significant Figures

**1. When the first digit after the last significant figure is less than 5,** simply cut off all extra figures without changing the last significant figure.

**Example:**

A calculation gives the number 3.9634263 for a value that should have four significant figures. The fifth digit (which is the first nonsignificant figure) is 4, which is less than 5. Therefore, the value is correctly given as **3.963**.

**2. When the first digit after the last significant figure is greater than 5,** add 1 to the last significant figure and drop all following digits.

**Example:**

A calculation gives the number 0.0462733 for a value that should have three significant figures. The first nonsignificant figure is 7 (the zeroes in front of the 4 serve only to locate the decimal point and do not count as significant figures), which is greater than 5. Therefore, the value is correctly given as **0.0463**.

**3. When the first digit after the last significant figure is equal to 5,** the situation is ambiguous and there is no universally accepted way to handle this case. A good guide to follow is:

- a. Look at the *second* digit after the last significant figure. If it is larger than 5, round the last significant figure upward by adding 1 to it. If it is 5 or smaller, or if there is no second nonsignificant figure, go to step b.
- b. When the first digit after the last significant figure is equal to 5, and the second digit after the last significant figure offers no basis for rounding upward, as explained in a, always round the last significant figure to the nearest *even* number. This offsets any psychological bias for rounding in a non-random manner, since there is an equal probability that choosing the next nearest even number results in rounding up or down.

**Example:**

a. A calculation gives the number 123.6257 for a value that should have five significant figures. The first non-significant figure is 5, which is ambiguous with respect to rounding up or down. Because the second non-significant figure is 7, which is larger than 5, the last significant figure should be rounded upward by adding 1. The value is correctly given as **123.63**.

b. A calculation gives the number 3.775 for a value that should have three significant figures. The correct value could be either 3.77 or 3.78, since 3.775 is exactly in the middle between them. By choosing the closest *even* number, the value is correctly given as **3.78**.

## Rules for Finding the Correct Number of Significant Figures

An exact treatment for finding the correct number of significant figures is more complicated than necessary for most situations. If you remember that **no mathematical operation can increase the precision of an experimental result**, you can use three simple rules for determining the correct number of significant figures.

**1. When the precision of a number has been determined**, as the standard or average deviation, the average value of a series of measurements should have the same number of decimal places as the  $\pm$  value of the deviation.

**Example:**

The molarity of permanganate solution in Example 1 has an average deviation of  $\pm 0.0003$ . Therefore, the average value of the molarity should contain four figures after the decimal point. In calculating the average, the calculator result of

$$0.4057/4 = 0.101425000 \text{ mol/L}$$

must be rounded to **0.1014 mol/L** in order to use significant figures correctly.

**2. If a value is calculated using multiplication and/or division**, the value should be rounded off to have the same number of significant figures (regardless of the position of the decimal point) as the quantity used in the calculation that has the least number of significant figures.

**Example:**

The velocity of a rolling ball is determined by observing that it rolls 135.6 cm in 12.1 seconds. Using a calculator, the velocity found to be:

$$(135.6 \text{ cm})/(12.1 \text{ s}) = 11.20661157 \text{ cm/s}$$

Because the time measurement, 12.1 seconds, has only three significant figures, the answer is limited to three significant figures. The answer is expressed correctly as **11.2 cm/s**.

**3. If a value is calculated using addition and/or subtraction**, the value should be rounded off to have the same number of *digits after the decimal point* as the quantity used in the calculation that has the least number of digits after its decimal point.

**Example:**

$$\begin{array}{r} 265.3 \\ 33.67 \\ 1.0983 \\ \hline 300.0683 \end{array}$$

Because 265.3 has only one digit after the decimal point, the answer must be rounded off to just one decimal place, as indicated by the vertical line. The answer is correctly given as **300.1**.

$$\begin{array}{r} 34.694 \\ -34.63 \\ \hline 0.064 \end{array}$$

Because 34.63 has only two digits after the decimal point, the answer must be rounded off to two decimal places. The answer is correctly given as **0.06**.