# ANALYSIS OF ERRORS

Precision and Accuracy

Two terms are commonly associated with any discussion of error: "precision" and "accuracy". **Precision** refers to the reproducibility of a measurement while **accuracy** is a measure of the closeness to true value. The concepts of precision and accuracy are demonstrated by the series of targets below. If the center of the target is the "true value", then **A** is neither precise nor accurate. Target **B** is *precise* (reproducible) but not accurate. The average of target **C**'s marks give an *accurate* result but precision is poor. Target **D** demonstrates both *precision* and *accuracy* - which is the goal in lab.

A   B   C   D
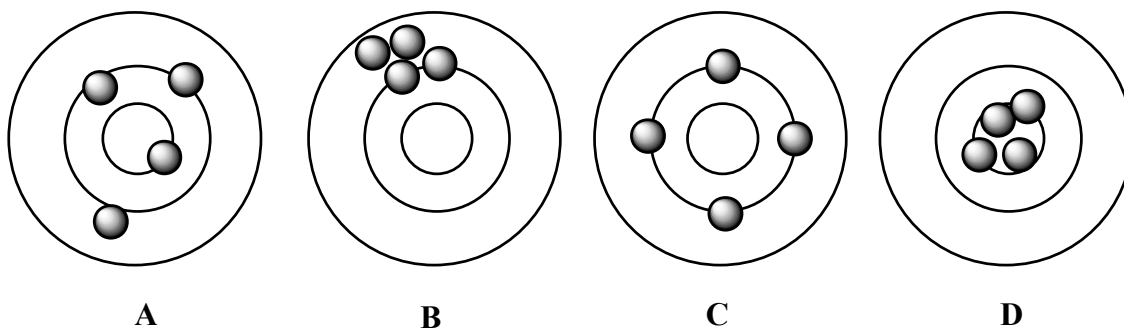
All experiments, no matter how meticulously planned and executed, have some degree of error or uncertainty. In general chemistry lab, you should learn how to identify, correct, and evaluate sources of error in an experiment and how to express the accuracy and precision of measurements when collecting data or reporting results.

Errors

Three general types of errors occur in lab measurements: random error, systematic error, and gross errors.

Random (or indeterminate) errors are caused by uncontrollable fluctuations in variables that affect experimental results. For example, air fluctuations occurring as students open and close lab doors cause changes in pressure readings. A sufficient number of measurements result in evenly distributed data scattered around an average value or mean. This positive and negative

scattering of data is characteristic of random errors. The **estimated standard deviation** (the error range for a data set) is often reported with measurements because random errors are difficult to eliminate. Also, a "best-fit line" is drawn through graphed data in order to "smooth out" random error.

Systematic (or determinate) errors are instrumental, methodological, or personal mistakes causing "lopsided" data, which is consistently deviated in one direction from the true value. Examples of systematic errors: an *instrumental error* results when a spectrometer drifts away from calibrated settings; a *methodological error* is created by using the wrong indicator for an acid-base titration; and, a *personal error* occurs when an experimenter records only even numbers for the last digit of buret volumes. Systematic errors can be identified and eliminated after careful inspection of the experimental methods, cross-calibration of instruments, and examination of techniques.

Gross errors are caused by experimenter carelessness or equipment failure. These "outliers" are so far above or below the true value that they are usually discarded when assessing data. The "Q-Test" (discussed later) is a systematic way to determine if a data point should be discarded.

Precision of a Set of Measurements

A data set of repetitive measurements is often expressed as a single representative number called the mean or average. The **mean** ($\overline{x}$) is the <u>sum of individual measurements</u> (x_i) divided by the <u>number of measurements</u> (N).

(1)

$$\overline{x} = \frac{\sum x_i}{N} \qquad \text{(mean)}$$

Precision (reproducibility) is quantified by calculating the average deviation (for data sets with 4 or fewer repetitive measurements) or the standard deviation (for data sets with 5 or more measurements). Precision is the opposite of uncertainty Widely scattered data results in a *large* average or standard deviation indicating *poor precision*. Note: Both calculations contain the

deviation from the mean ($x_i - \bar{x}$), the difference between the individual experimental value and the mean value.

The **average deviation**, $\Delta\bar{x}$, is used when a data set contains less than 5 repetitive measurements. A small average deviation indicates data points clustered closely around the mean and good precision.

(2)
$$\Delta\bar{x} = \pm\frac{\sum|x_i - \bar{x}|}{N} \qquad \text{(average deviation, } N \le 4\text{)}$$

The absolute value is taken of the deviation from the mean, $|x_i - \bar{x}|$, so no information is gained about the direction of the error. The **relative average deviation** is the average deviation divided by the average and then expressed as a percentage: $\dfrac{\Delta\bar{x}}{\bar{x}} \times 100$.

For data sets with 5 or more measurements, the **estimated standard deviation** (s), is used to express the precision of the measurements. The **number of degrees of freedom** ($N-1$) is the total number of measurements minus one. Estimated standard deviation is used frequently in lab when students pool their data.

(3)
$$s = \pm\sqrt{\frac{\sum(x_i - \bar{x})^2}{N-1}} \qquad \text{(estimated standard deviation, } N \ge 5\text{)}$$

Example: Student A recorded the volume of a gas at 1.0 atm and 23 °C in experiments 1-4. Student B recorded the volume of a gas at 1.0 atm and 23 °C in experiments 5-8.

Student A		Student B	
Expt #	**Volume (L)**	**Expt #**	**Volume (L)**
1	26.05	5	26.02
2	26.18	6	26.27
3	26.30	7	26.17
4	26.20	8	26.22

Precision of Student A's Data:

Mean Volume: $\bar{v} = \dfrac{26.05 + 26.18 + 26.30 + 26.20}{4} = 26.18$ Liters

Average Deviation: $\Delta\bar{x} = \pm \dfrac{|\,0.13 + 0.00 + 0.12 + 0.02\,|}{4} = \pm 0.068$

Relative Average Deviation: $\%\Delta\bar{x} = \pm 0.068/26.18\ \text{L} \times 100 = 0.26\%$

The average deviation for Student A's data is (± 0.068). Therefore, the volume is reported as 26.18 ± 0.068 L.

Precision of All Data:

Mean Volume: $\bar{v} = \dfrac{26.05 + 26.18 + 26.30 + 26.20 + 26.02 + 26.27 + 26.17 + 26.22}{8} = 26.18$ L

Estimated Standard Deviation:

$$s = \pm \sqrt{\dfrac{0.0169 + 0.000 + 0.0144 + 0.0004 + 0.0256 + 0.0081 + 0.0001 + 0.0016}{8 - 1}} = \pm 0.10$$

The estimated standard deviation for the entire set of data is (± 0.10). Therefore, the volume is reported as 26.18 ± 0.10 L.

Error Propagation

When combining measurements with standard deviations in mathematical operations, the answer's standard deviation is a combination of the standard deviations of the initial measurements. In other words, the error is "propagated".

The following examples demonstrate error propagation for addition/subtraction and multiplication/division. To calculate the resultant standard deviation use the formulas below where A, B, and C represent experimental measurements and a, b, and c are the respective standard deviations for each measurement:

(4)

$$(A \pm a) \pm (B \pm b) \pm (C \pm c) \ = \ (A \pm B \pm C) \pm \sqrt{a^2 + b^2 + c^2}$$

(addition / subtraction)

Example:

$$(2.0 \pm 0.2) - (1.0 \pm 0.1) + (3.0 \pm 0.3) \ = \ 4.0 \pm ?$$

$$= \ (2.0 - 1.0 + 3.0) \pm \sqrt{0.2^2 + 0.1^2 + 0.3^2} \ = \ 4.0 \pm 0.4$$

(5)

$$\frac{(A \pm a) \times (B \pm b)}{(C \pm c)} \ = \left(\frac{AB}{C}\right) \pm \left(\frac{AB}{C}\right) \sqrt{\left(\frac{a}{A}\right)^2 + \left(\frac{b}{B}\right)^2 + \left(\frac{c}{C}\right)^2}$$

(multiplication / division)

Example:

$$\frac{(2.0 \pm 0.2) \times (1.0 \pm 0.1)}{(3.0 \pm 0.3)} \ = \ \left(\frac{2.0 \times 1.0}{3.0}\right) \pm ?$$

$$\left(\frac{2.0 \times 1.0}{3.0}\right) \pm \left(\frac{2.0 \times 1.0}{3.0}\right) \sqrt{\left(\frac{0.2}{2.0}\right)^2 + \left(\frac{0.1}{1.0}\right)^2 + \left(\frac{0.3}{3.0}\right)^2} \ = \ 0.67 \pm 0.12$$

Accuracy of a Result

The accuracy of a result can be quantified by calculating the **percent error**. The percent error can only be found if the *true value* is known. Although the percent error is usually written as an *absolute value*, it can be expressed a negative or positive sign to indicate the direction of error from true value.

(6)

$$\% \text{ Error} \ = \ \frac{(\text{true value - experimental value})}{\text{true value}} \times 100 \qquad (\text{percent error})$$

Assume the true value for the gas volume was 26.04 L in the previous example. Then the error in the measurements is 0.54%

$$\% \text{ Error} = \frac{(26.04 - 26.18)}{26.04} \times 100 = 0.54\%$$

The Q-Test for Rejecting Data

As mentioned previously, **outliers** are data measurements occurring from *gross errors*. Their value deviates significantly from the mean. The Q-Test can be used to determine whether an individual measurement should be rejected or retained.

The quantity Q is the absolute difference between the <u>questioned measurement</u> (x_q) and the <u>next closest measurement</u> (x_n) divided by the <u>spread</u> (ω), *the difference between the largest and smallest measurement*, of the entire set of data.

(7)

$$Q = \frac{(x_q - x_n)}{\omega}$$

Q is compared to a specified **confidence levels** (the percent probability a measurement will fall into a range around the mean (x).) If Q is greater than the values listed below for a particular confidence level, the measurement should be rejected. If Q is less than the values in the table, the measurement should be retained.

Number of Observations	The Q-Test for Rejecting Data		
	Confidence Levels		
	90%	96%	99%
3	0.94	0.98	0.99
4	0.76	0.85	0.93
5	0.64	0.73	0.82
6	0.56	0.64	0.74
7	0.51	0.59	0.68
8	0.47	0.54	0.63
9	0.44	0.51	0.60
>9	0.41	0.48	0.57

Assume the student measuring the gas volumes collected a ninth measurement equal to 27.58 L. The Q-value for this measurement is calculated as follows:

Q-value:

$$Q = \frac{27.58 - 26.30}{27.58 - 26.05} = 0.82$$

The limiting value is 0.60 for rejecting data at the 99% confidence level for 9 measurements. Since 0.82 is greater than 0.60, the student should reject the measurement.

* A shortcut can be used to test a suspect measurement: Calculate the mean and average or standard deviation without using the suspect measurement and reject the suspect measurement if its deviation from the mean is greater than four times the average or standard deviation.

Example: The mean and standard deviation of the original eight gas volume measurements is 26.18 ± 0.10. Multiplying 0.10 by 4 gives 0.40. The deviation of the 9th suspect measurement is $27.58 — 26.18 = 1.40$ which is much greater than 0.40. Again, the student should reject the measurement.

Although a set of measurements may have very small standard deviations (high precision), the calculated results can be inaccurate because of systematic error. At the same time, experimental measurements with large standard deviations (poor precision) from random errors can still give an averaged result close to true value. A good experimenter sets his goals on both precision and accuracy when making measurements.

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Measurement Good Practice Guide: A Beginner's Guide to Uncertainty of Measurement:
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