Average, Deviation, and Standard Deviation

In experimental chemistry we generally determine the value of a measured quantity by repeated measurement. We assume that any errors in our measurements are random, meaning that it is equally likely that our measured results will be higher or lower than the "true value" we are seeking to determine. In other words, we assume that the set of all data has a central tendency, which we could express as an average. Actually, there are several ways of calculating this central tendency, but the simplest and most often used is the *arithmetic mean*, which is routinely called the average. For a set of N measurements of some quantity x, the arithmetic mean, $\bar{x}$, is defined as the sum of all the data divided by N:

$$\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N} = \frac{x_1 + x_2 + ... + x_N}{N}$$

We are often interested in the *precision* of our result; i.e., the repeatability of the measurements. A simple way of assessing the variation from the average of the data is to calculate the *deviation*. If $x_1, x_2, x_3 ...$ represent the individual measured quantities and $\bar{x}$ the arithmetic mean, then the individual deviations, d_i, are calculated as the differences between each data value and the mean:

$$d_1 = x_1 - \bar{x}$$
$$d_2 = x_2 - \bar{x}$$
$$d_3 = x_3 - \bar{x}$$
$$...$$

Note that if the measured value is less than the mean, the deviation is negative, and if the measured value is greater than the mean, the deviation is positive. For sufficiently large data sets, the algebraic sum of all the deviations should be zero, within the limits of rounding and significant digits.

The arithmetic mean of the magnitudes (without sign) of all the deviations is sometimes used as an indicator of the precision of the data. However, most scientists prefer to use a statistical indicator of the precision, the calculated *standard deviation*, also called the *standard error*. For typical laboratory measurements there is generally no limit on the number of pieces of data that could be collected, given enough time and patience, so there is no fixed population of numbers, all of which we are obtaining. In a situation like this, we can only calculate an *estimated standard deviation*, based on the limited set of data obtained. This estimated standard deviation, s, is calculated by taking the sum of the squares of the individual deviations, d_i^2, dividing by one less than the number of pieces of data, $N-1$, and then taking the square root of the result:

$$s = \sqrt{\frac{\sum_{i=1}^{N} d_i^2}{N-1}} = \sqrt{\frac{d_1^2 + d_2^2 + ... + d_N^2}{N-1}}$$

The calculated value of the estimated standard deviation is customarily appended to the mean for the data, preceded by a plus and minus sign; e.g., $\bar{x} \pm s$. When using this format, the number of

decimal places in the standard deviation should be the same as the number of decimal places appropriate to the arithmetic mean for the data. For example, suppose the mean for the data is 2.356 and the standard deviation is calculated to be 0.005732; then, the result would be written as 2.356 ± 0.006.

The significance of the standard deviation for a measured quantity can be understood in terms of the *normal distribution curve* expected for a large number of repeated measurements subject to random error. The frequency with which a deviation of a certain magnitude should occur (its probability, *P*) is predicted by the equation

$$P \; = \; \frac{1}{s\sqrt{2\pi}} e^{-d^2/2s^2}$$

in which *e* is the base of the natural logarithm. This equation gives the so-called "bell-shaped curve" shown below.

Normal Distribution Curve

Frequency of Deviation

-3   -2   -1   0   1   2   3

Standard Deviations from Mean
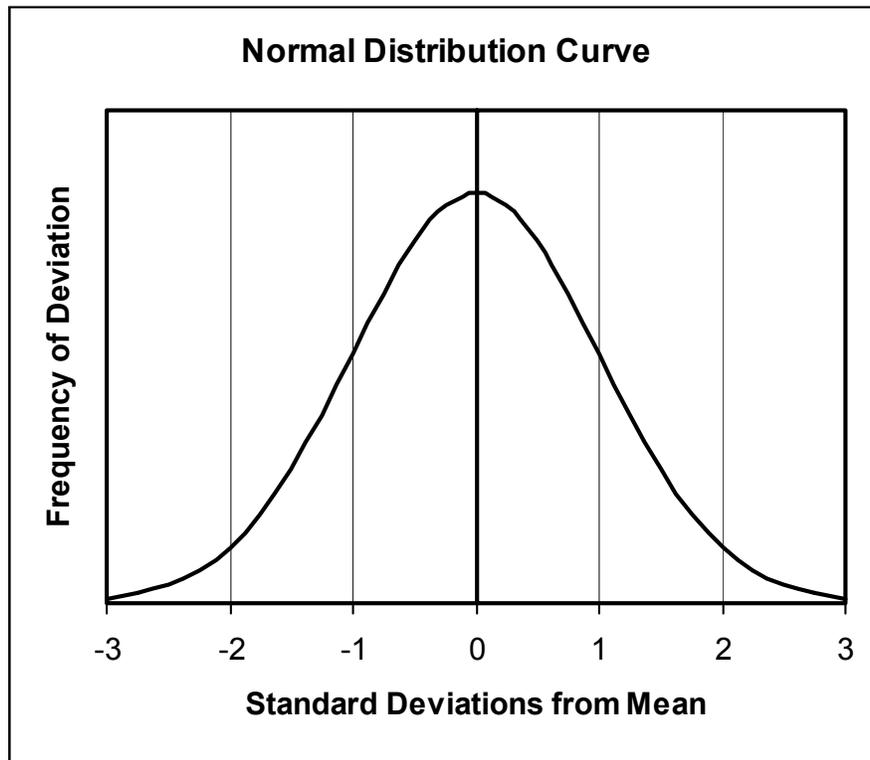
This curve predicts that the most probable observed value is that of the mean (zero deviation). Larger deviations from the mean, either positive or negative, become less likely as their magnitudes increase. In terms of the calculated standard deviation, 68% of the measurements should fall within a range of $\bar{x} \pm s$, 95% should fall within $\bar{x} \pm 2s$, and 99% should fall within $\bar{x} \pm 2.5s$. Hence, the smaller the standard deviation, the more closely the measured values tend to cluster about the mean, indicating better precision. A statement of the standard deviation, then, gives us some confidence in the reliability of our measurements.