

TOPICS

- Units
- Dimensions
- Conversions
- Dimensionless Groups
- Precision and Accuracy, Significant Figures
- Statistical Analysis of Data

Fundamental dimensions: mass, length, time, temperature

Derived Quantities	Fundamental Quantities	English	SI (mks)	cgs
	length	foot (ft)	meter (m)	centimeter (cm)
	mass	pound mass (lb _m)	kilogram (kg)	gram (g)
	time	second (s)	s	s
volume	length ³	gallon = 0.133 ft ³	m ³	cm ³
force	(mass)(length)/time ²	lb _f = 32.174 lb _m ft/s ²	Newton (N) = 1 kg•m/s ²	dyne = 1 g•cm/s ²
pressure	force/area = mass/(length)(time ²)	1 psi = 1 lb _f /in ²	Pascal (Pa) = 1 N/m ² = 1 kg/(m•s ²)	1 dyne/cm ² = 1 g/(cm•s ²)
concentration	mass/volume = mass/(length) ³	lbm/ft ³	kg/m ³	g/cm ³

Note on temperature: absolute vs. relative

Relative temperatures are expressed in °F or °C. These are relative in the sense that °F and °C are defined relative to an arbitrary reference state, e.g. water freezes at 0°C and boils at 100°C at atmospheric pressure.

Absolute temperatures are defined relative to absolute zero. Absolute temperature scales are degrees Rankine (°R) for the English system and Kelvin (K, note there is no ° symbol for Kelvin) for the SI and cgs systems.

$$\text{value in } ^\circ\text{R} = \text{value in } ^\circ\text{F} + 459.69$$

$$\text{value in K} = \text{value in } ^\circ\text{C} + 273.15$$

Always use absolute temperature in calculations!!

Most commonly used SI prefixes

$$\text{nano (n)} = 10^{-9}$$

$$\text{micro } (\mu) = 10^{-6}$$

$$\text{milli (m)} = 10^{-3}$$

$$\text{centi (c)} = 10^{-2}$$

$$\text{deci (d)} = 10^{-1}$$

$$\text{kilo (k)} = 10^3$$

$$\text{mega (M)} = 10^6$$

$$\text{giga (G)} = 10^9$$

Unit Conversions: “Dimensional Equations”

$$(75\text{kg}) \left\langle \frac{1000\text{g}}{\text{kg}} \right\rangle = 75,000\text{g} = 7.5 \times 10^4\text{g}$$

$$(1.0\text{psi}) \left\langle \frac{101.325\text{kPa}}{14.7\text{psi}} \right\rangle = 6.9\text{kPa}$$

...because I knew that 1 atmosphere = 14.7 psi = 101.325 kPa

Rules for using units in equations

1. All terms in sums (or differences) (a+b) must have the same units.
2. The product (or quotient) of two or more terms have units equal to the product (or quotient) of the units of each term: units of ab [=] (units of a)(units of b)

$$F = ma \quad F [=] (\text{mass})(\text{length})/\text{time}^2$$

3. Both sides of an equation must have the same units.
4. Arguments of transcendental functions must be dimensionless (unitless), e.g. a must be dimensionless in

$$\exp(a) (= e^a) \quad \sin(a) \quad \ln(a)$$

example

Transition state theory says that the rate constant of a chemical reaction is given by

$$k = k_o \exp(-E_a / RT)$$

where R is the universal gas constant R = 8.314 joule/mole K. If T is given in K, and k is given in units of 1/s, then k_o must be in units of 1/s and E_a must be in units of RT [=] joule/mole.

example

What is the force experienced by a 20 lb_m object accelerated at 4.0 m/s²?

solution: Use Newton's law $F = ma$

$$F = (20lb_m) \left(4.0 \frac{m}{s^2} \right) = 80lb_m \bullet m / s^2, \text{ what's a "lbm} \bullet m/s^2\text{?"}$$

$$F = (20lb_m) \left(4.0 \frac{m}{s^2} \right) \left\langle \frac{453.6g}{lb_m} \right\rangle \left\langle \frac{1lb_f}{32.174lb_m ft / s^2} \right\rangle \left\langle \frac{1ft}{0.3048m} \right\rangle = 8.1577lb_f$$

But, as we'll see below, we only have the right to express this answer as 8.2 lb_f.

OR we could have handled this by first converting mass from the annoying English system to the convenient SI system

$$(20lb_m) \left\langle \frac{453.6g}{lb_m} \right\rangle \left\langle \frac{1kg}{1000g} \right\rangle = 9.1kg$$

Then

$$F = (9.1kg) \left(4.0 \frac{m}{s^2} \right) = 36 \frac{kg \bullet m}{s^2} = 36N$$

Check conversion

$$(36N) \left\langle \frac{0.2248lb_f}{N} \right\rangle = 8.2lb_f$$

Problem...

A simple model for the pressure of a gas is

$$P = \frac{RT}{v - b}$$

Suppose temperature T [=] K, pressure p [=] atm and molar volume v [=] L/mole.

What are the units of b?

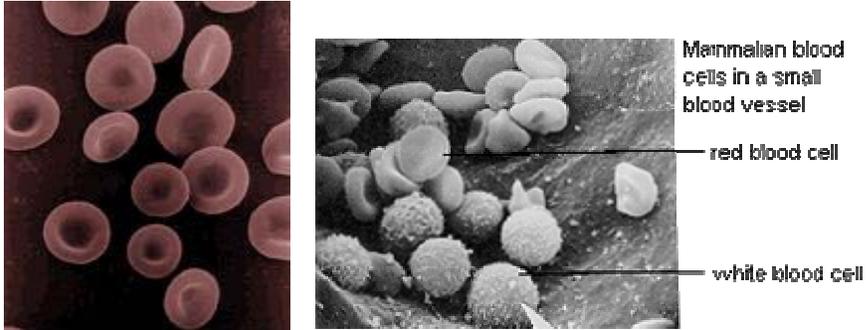
What are the units of R?

Dimensionless Groups

Provide a numerical description of a system or of system behavior without knowing the details of the system... based on groupings (products and quotients) of system parameters where the units of the groupings cancel out.

Example: aspect ratio... of red blood cells

RBCs are biconcave disks with a diameter, d , of $\sim 8 \mu\text{m}$ and thickness, t , of $\sim 2 \mu\text{m}$



Aspect ratio = $d/t = 8 \mu\text{m}/2 \mu\text{m} = 4$ Note the units cancel out – the aspect ratio is a dimensionless group.

What looks similar to a RBC – a Frisbee? A hockey puck?

Example: Reynolds number

Consider the flow of a fluid in a closed, circular conduit – e.g. blood flowing in a vein

How can we characterize the flow?

What governs the pressure change (drop), $\Delta P = P_{in} - P_{out}$ from inlet to outlet?

Important properties of conduit and fluid flowing in conduit:

pressure drop, ΔP [=] force/area [=] $\text{mass} \cdot \text{length} / ((\text{time})^2 \cdot (\text{length})^2)$

diameter, d [=] length

length, L [=] length

average fluid velocity, $\langle v \rangle$ [=] length/time

fluid density, ρ [=] mass/volume [=] $\text{mass} / (\text{length})^3$

fluid viscosity, μ [=] $\text{mass} / ((\text{length}) \cdot (\text{time}))$

How many independent dimensionless groups can be formed from these system parameters?

$$\begin{aligned} \# \text{ independent dim'less groups} &= (\# \text{ parameters}) - (\# \text{ types of dimensions}) \\ &= 6 (\Delta P, d, L, \langle v \rangle, \rho, \mu) - 3 (\text{length, time, mass}) \\ &= 3 \end{aligned}$$

dimensionless groups for this system:

#1: aspect ratio, L/d [=] length/length [=] dim'less

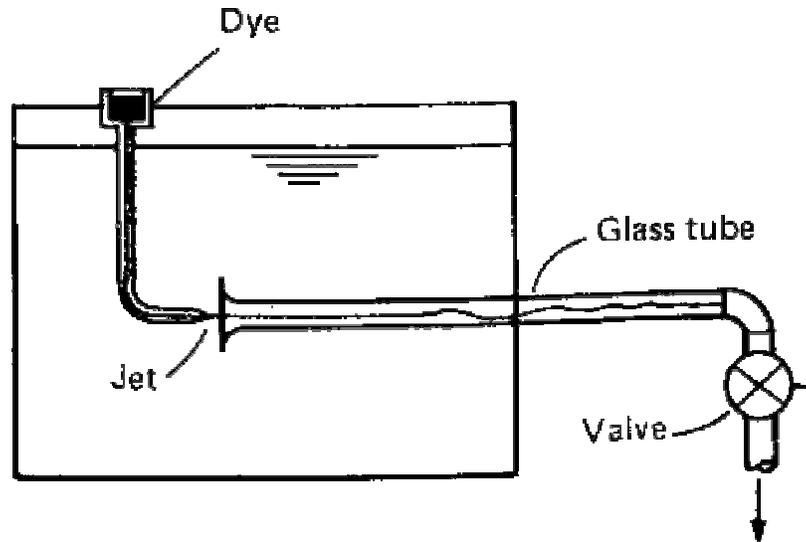
(or d/L 1/aspect ratio)

#2 & #3: ??

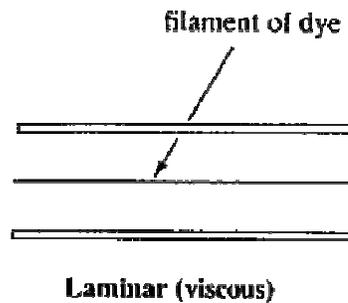
Dimensionless groups characterize the behavior of the system

Reynolds number governs flow type.

The Osbourne Reynolds experiment of the 1880s...



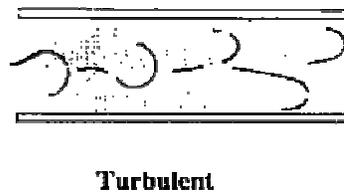
At $Re < \sim 2100$, the flow is laminar



At $\sim 2100 < Re < 4000$, the flow is transitional



At $Re > 4000$, the flow is turbulent



From:

<http://www.cartage.org.lb/en/themes/Sciences/Physics/Mechanics/FluidMechanics/RealFluids/Laminar/Laminar.htm>

Further, Re may be used to correlate the ΔP behavior

The Buckingham Pi theorem for dimensionless groups state that if we have identified all the independent dimensionless groups for a system, we may write any one of the dimensionless groups as a function of all the remaining dimensionless groups. If we denote a dimensionless group with the symbol Π :

$$\begin{aligned}\Pi_1 &= f(\Pi_2, \Pi_3, \Pi_4, \dots \text{ etc}) \text{ or} \\ \Pi_2 &= g(\Pi_1, \Pi_3, \Pi_4, \dots \text{ etc}) \text{ or} \\ \Pi_3 &= h(\Pi_1, \Pi_2, \Pi_4, \dots \text{ etc}) \dots\end{aligned}$$

Buckingham Pi theory, unfortunately, does not tell us what the functions f , g , and h are, unfortunately. BUT, the generic power law form

$$\Pi_1 = a\Pi_2^b\Pi_3^c\Pi_4^d \dots \text{ etc where } a, b, c, d \text{ are constants has proven very versatile.}$$

In the case of ΔP we can write

$$(\text{dim'less } \Delta P) = a(\text{Reynolds \#})^b(\text{aspect ratio})^c$$

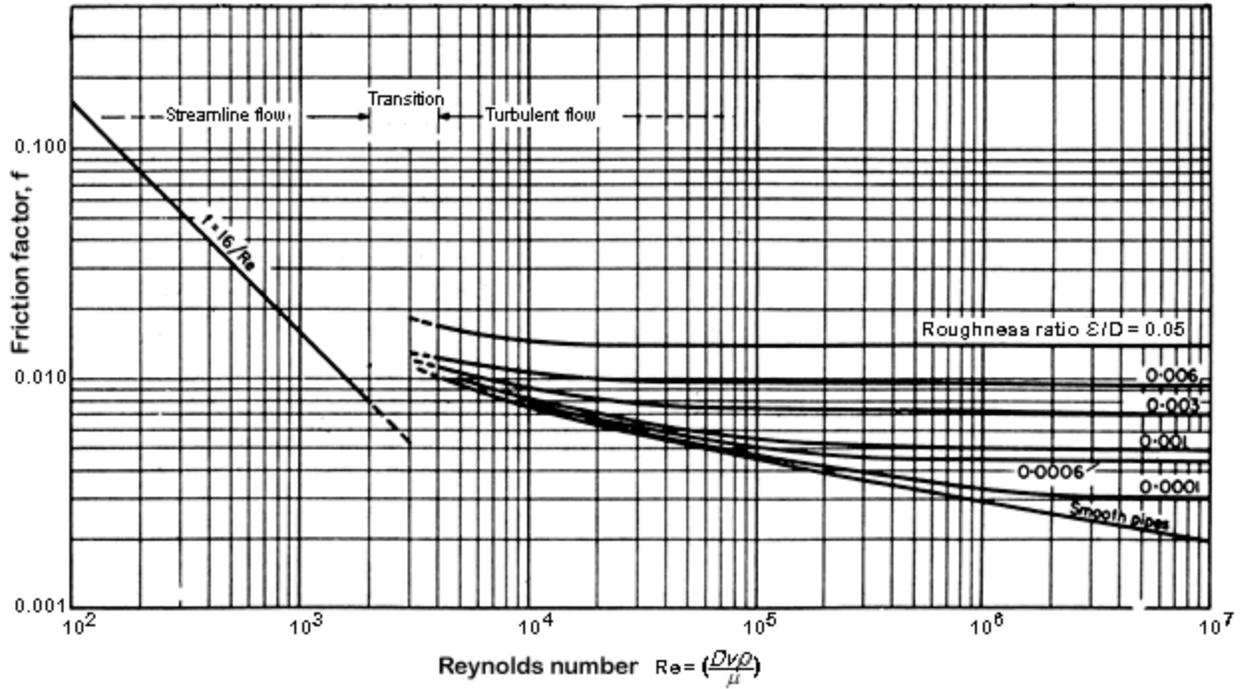
For laminar flow, theory and experiment have given an expression for ΔP , the Hagen-Poiseuille equation

$$\begin{aligned}(\Delta P/0.5\rho\langle v \rangle^2) &= 64(\mu/(\rho\langle v \rangle d))(L/d) \\ &= (\text{dim'less } \Delta P) = 64(\text{Reynolds \#})^{-1}(\text{aspect ratio})^1\end{aligned}$$

Rearranging,

$$\Delta P = 32\langle v \rangle \mu L/d^2$$

Further, ΔP depends on the flow type (and conduit roughness). Moody performed extensive experiments in the 1940s to characterize this behavior (summarized in figure below). Note that the friction factor, f , is proportional to ΔP .



Friction factors in pipe
 (After Moody, 1944)

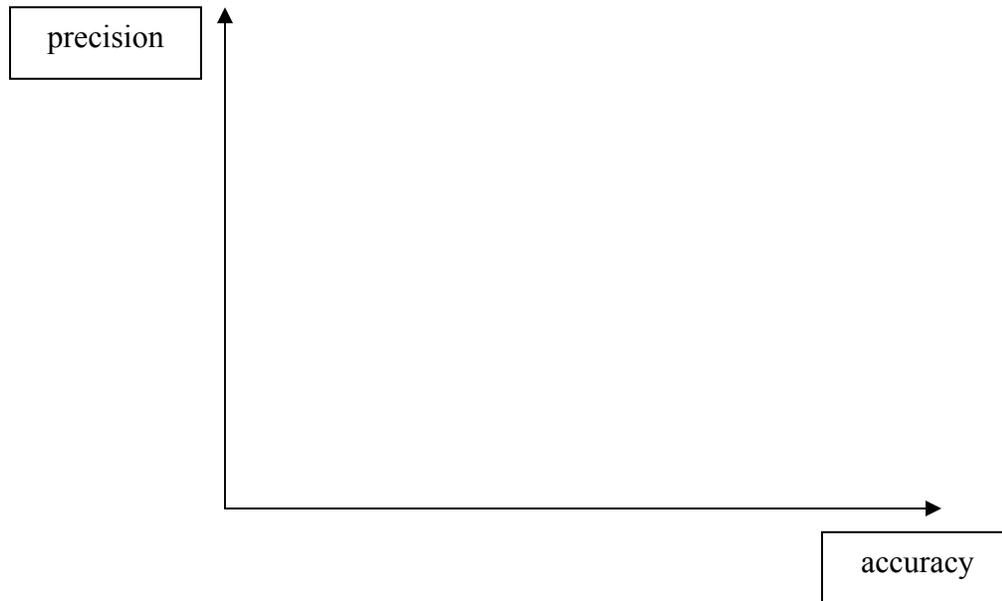
From: <http://www.nzfst.org.nz/unitoperations/flfltheory5.htm>

Suppose we explicitly consider conduit roughness, e.g. bumps with a length scale of e , and its effect on the flow. We can define another dimensionless group, e/d , the relative roughness and can write

$$(\text{dim'less } \Delta P) = a(\text{Reynolds \#})^b(\text{aspect ratio})^c(\text{relative roughness})^d \dots$$

Precision and Accuracy

precision = repeatability
accuracy = correctness



Imprecise data may be the result of instrumentation performance and/or operator care

Inaccurate data may be the result of instrument miscalibration, errors consistent errors in technique

Dealing with Precision in Calculations - Significant Figures and Precision

Significant figures are used to represent the certainty with which we know a quantity. Let's say we repeat a series of measurements many times, and there is some variability in our measurements. When we calculate the mean and standard deviation of our measurements, we find that the mean (in arbitrary units) is 1.756, and the standard deviation is 0.3. This means that we really are not sure about the digits in the hundredths place and beyond, and we should report our value as 1.8 ± 0.3 . Only digits up to the tenths place are significant.

Another way to look at this is to consider the precision of our measuring device. What if we use a ruler whose smallest markings are tenths of an inch. If we measure a length of 1.2 inches, we know that it could be somewhere between 1.15 and 1.25, but we can't measure that precisely with this ruler. So, we report 1.2 inches – we have two significant figures. In general we should not report a quantity with more significant figures than are allowed by the precision of our measurements.

Rule: The number of significant figures in a quantity is equal to the number of digits from the first non-zero digit on the left to either a) the last digit on the right (can be either 0 or non-zero) if there is a decimal point or b) the last non-zero digit on the right if there is no decimal point.

How many significant figures?

21.2	3 sig figs
172,000	3 sig figs
172,000.0	7 sig figs

Precision of calculated quantities (how many sig figs)

Follow this procedure:

1. Complete the calculation carrying excess precision (use all digits in every quantity in calculation). This avoids accumulating round-off error.
2. Determine the appropriate number of sig figs in the results by the following rules:
 - a. Addition or subtraction: The position of the poorest measurement (least precise number) governs:

2300
+ 170
<hr/>

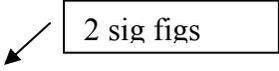
2470 the least precise number is in the hundreds place, so the result is 2500 (2 sig figs)

$$\begin{array}{r} 1530 \\ - 2.56 \\ \hline \end{array}$$

1527.44 → 1530 (and you thought you knew how to subtract...☺)

$$2.75 \times 10^6 + 3.4 \times 10^4 = (2.75 + 0.034) \times 10^6 = (2.784) \times 10^6 = (2.78) \times 10^6$$

b. Multiplication or division: The number of significant figures allowed in the product or quotient is determined by the number of sig figs in the factor that has the fewest sig figs.



$$(3.0)(7.1621) = 21.4863 = 21$$

Note on round-off rules

If the last digit is 5, then round to the nearest even number.

Express the following quantities with 2 sig figs:

$$3.65 \rightarrow 3.6$$

$$3.75 \rightarrow 3.8$$

$$3.751 \rightarrow 3.8$$

c. units conversion factors typically considered infinitely precise unless arbitrarily rounded-off

Example: compute k

$$k = k_0 \exp\{-E_A/RT\}$$

where

$$k_0 = 1.85 \times 10^{-7} \text{ 1/s}$$

$$E_A = 35 \text{ cal/mol}$$

$$T = 220 \text{ K}$$

$$R = 1.987 \text{ cal/(mol}\cdot\text{K)}$$

Precision and Statistical Analysis of Measurements

There are many good practical texts on statistical methods. This introductory treatment is based largely on Skoog and West, *Fundamentals of Analytical Chemistry* Saunders College Publishing, New York, 1976. A more thorough treatment can be found in Box, Hunter and Hunter, *Statistics for Experimenters*, John Wiley & Sons, New York, 1978. More extensive versions of tables in this lecture are available (e.g. CRC Handbook of Chemistry and Physics).

The Uses of Statistics

1. Definition of the interval around the mean of a set within which the true mean can be expected to be found with a certain probability.
2. Determination of the number of times a measurement should be replicated in order for the experimental mean to be included, with a certain probability, within a predetermined interval around the true mean.
3. Guidance concerning whether or not an outlying value in a set of replicate results should be retained or rejected in calculating a mean for the set.
4. Estimation of the probability that two samples analyzed by the same method are significantly different; that is, whether or not a difference in experimental results is likely to be a consequence of indeterminate (random) error or of a real difference in the samples or of a systematic error in measuring one of the samples.

Definitions

mean, arithmetic mean, average (\bar{x}): these are synonyms for the numerical value obtained by dividing the sum of a set of replicate measurements by the number of individual results in the set.

The mean of the set (4.0, 4.1, 4.2, 4.2, 4.4, 4.1) = (4.0+ 4.1+ 4.2+ 4.2+ 4.4+4.1)/6 = 4.2

median: that result within a set which is greater than half of the set and less than half of the set. For a set with an odd number of members, the median is found directly; for a set with an even number of members, the average of the central pair is taken.

The median of the set (4.0, 4.1, 4.2, 4.2, 4.4, 4.1) is found by first listing them in increasing order (4.0, 4.1, 4.1, 4.2, 4.2, 4.4). Since there is an even number of results, the median is (4.1+4.2)/2 = 4.15; but because of the number of significant figures we are allowed, we round this off to 4.2. The median does not necessarily equal the mean.

average deviation from the mean: if there are i members of a set, the average deviation from the mean is calculated as

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

where the vertical lines represent the absolute value.

The average deviation from the mean for the data set (4.0, 4.1, 4.2, 4.2, 4.4, 4.1) is

$$\frac{|4.0 - 4.2| + |4.1 - 4.2| + |4.2 - 4.2| + |4.2 - 4.2| + |4.4 - 4.2| + |4.1 - 4.2|}{6}$$

$$= \frac{0.2 + 0.1 + 0 + 0 + 0.2 + 0.1}{6} = 0.1$$

Sometimes we use a relative method to express precision.

The relative deviation from the mean is simply the average deviation from the mean divided by the mean ($0.1/4.2 = 2\%$)

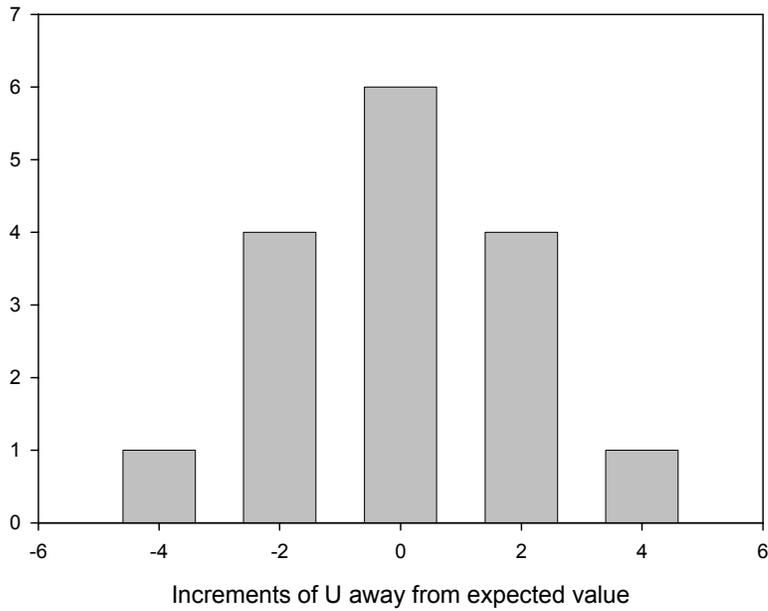
The most important measure of precision is the standard deviation, discussed below.

The Normal Curve

To qualitatively understand the expected distribution of measurements around the mean, let's suppose we make a series of measurements, and there are four possible types of random errors (uncertainties) that can be made. We'll call these U_1 , U_2 , U_3 and U_4 . Each of these uncertainties causes the value we measure to be either $+U$ above the expected value or $-U$ below the expected value. Consider all the possible ways these four uncertainties can be combined in any one measurement, tabulated below:

Combination of Uncertainties	Magnitude of Indeterminate Error	Frequency of Occurrence
$+U_1+U_2+U_3+U_4$	$4U$	1
$-U_1+U_2+U_3+U_4$ $+U_1-U_2+U_3+U_4$ $+U_1+U_2-U_3+U_4$ $+U_1+U_2+U_3-U_4$	$2U$	4
$-U_1-U_2+U_3+U_4$ $+U_1+U_2-U_3-U_4$ $+U_1-U_2+U_3-U_4$ $-U_1+U_2+U_3-U_4$ $+U_1-U_2-U_3+U_4$	0	6
$+U_1-U_2-U_3-U_4$ $-U_1+U_2-U_3-U_4$ $-U_1-U_2+U_3-U_4$ $-U_1-U_2-U_3+U_4$	$-2U$	4
$-U_1-U_2-U_3-U_4$	$-4U$	1

If we plotted this as a histogram it would look like this. (a binomial distribution...)



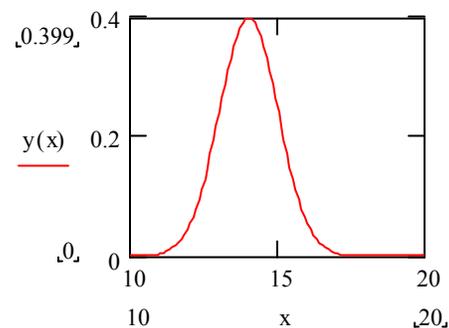
For a large number of measurements, plots of measurements x with random errors such as this are represented mathematically by the *normal curve*, where the frequency of occurrence y is

$$y = \frac{\exp\left(\frac{-(x - \mu)^2}{2\sigma^2}\right)}{\sigma\sqrt{2\pi}}$$

where μ is the true or expected mean. The parameter σ is the *standard deviation*. The breadth of the distribution is directly related to the standard deviation.

Here is the normal curve for a set of measurements with mean 14 and standard deviation 1.0

It can be shown that 68.3% of the area under the curve, or 68.3% of all the measurements will fall within 1 standard deviation ($\pm 1\sigma$) from the mean. 95.5% of the measurements will fall within $\pm 2\sigma$ of the mean, and 99.7% will fall within $\pm 3\sigma$.



The standard deviation is calculated from a set of N measurements as

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (x_i - \mu)^2}{N}}$$

s is an expression of the width of the distribution. In fact, the “full width at half maximum” or FWHM is given by

$$\text{FWHM} = \sigma\sqrt{8 \ln 2}$$

variance: Often people will use the variance to express the precision of their measurements. The variance is equal to σ^2 .

standard error: S.E. = s / \sqrt{N}

Analysis of Small Sets of Data

For samples containing only 2 to ~ 20 measurements, the use of the normal curve with the standard deviation as calculated above, misrepresents the true precision of the data. This has to do with the fact that our measured mean is probably not exactly equal to the expected (or true) mean.

Illustration: The table below shows data for the calibration of a 10 mL pipette. Each entry is a measurement of the volume of water actually delivered from the 10 mL pipette.

Trial #	Volume (mL)	Trial #	Volume (mL)	Trial #	Volume (mL)
1	9.990	9	9.988	17	9.977
2	9.993	10	9.976	18	9.982
3	9.973	11	9.981	19	9.974
4	9.980	12	9.974	20	9.985
5	9.982	13	9.970	21	9.987
6	9.988	14	9.989	22	9.982
7	9.985	15	9.981	23	9.979
8	9.970	16	9.985	24	9.988

The mean and standard deviation for the entire data set (trials 1- 24) are $\bar{x}=9.982$ mL and $\sigma = 0.0063$.

If we instead analyze trials 1 – 12, ($\bar{x}=9.982$ mL and $\sigma = 0.0070$), and then we analyze trials 13 – 24 ($\bar{x}=9.982$ mL and $\sigma = 0.0056$) and take the means we get mean $\bar{x}=9.982$ mL and mean $\sigma = 0.0063$. We see that the mean of the standard deviations is close to the standard deviation of the full data set, but the individual standard deviations of the two subsets can vary quite a lot.

We make the situation worse by considering smaller subsets

Trials	mean	standard deviation
1-3	9.985	0.0088
4-6	9.983	0.0034
7-9	9.981	0.0079
10-12	9.977	0.0029
13-15	9.980	0.0078
16-18	9.981	0.0033
19-21	9.982	0.0057
22-24	9.983	0.0037
mean	9.982	0.0054

Notice how much the individual subset standard deviations fluctuate, and how much the mean of those standard deviations differs from the standard deviation of the full 24 trial data set. *It tends to be the case that the standard deviation from small subsets is too small.*

This negative bias in the standard deviation for small data sets is largely eliminated by calculating the standard deviation as

$$s = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N - 1}}$$

It is customary to call this s instead of σ to emphasize that this is an approximation of the true standard deviation because it is based on a small data set. Note also that we use the measured mean \bar{x} instead of the expected mean μ .

Confidence Intervals

The true mean can never be known with 100% certainty. The concept of the confidence interval (or confidence limits) is that it establishes a range of values around the measured mean, within which we can expect to find the true mean with some probability.

To be 100% certain that the true mean lies within our confidence interval, the interval has to be huge (infinite, really), so all possible values are included. That is worthless. We typically declare that we are satisfied to know that we can be 99%, or 95% certain that the true mean lies within our confidence interval.

If s is a good approximation of σ , confidence limits are set as follows. For any particular value of σ (approximated as s), the area under any part of the normal curve, relative to the total area under the curve can be related to a quantity z ,

$$z = \frac{x - \mu}{\sigma}$$

This ratio of areas is the *confidence level*, as it measures the probability for the absolute deviation $(x - \mu)$ being less than $z\sigma$. Put another way, for a given measurement x , z is essentially the number of standard deviations x is away from the true mean m .

Tables are available for the confidence levels for various values of z as a function of the confidence level or probability, P .

Confidence Level, %	$z(P)$
50	0.67
68	1.00
80	1.29
90	1.64
95	1.96
96	2.00
99	2.58
99.7	3.00
99.9	3.29

Thus, we can be 99% certain that the true mean will lie between our measured value $\pm 2.58\sigma$.

For a single measurement x , the confidence limit for $\mu = x \pm z(P)\sigma$. This is useful when the standard deviation is known for a particular type of measurement on a particular instrument. In other words, if you have a lot of experience using the instrument for the type of measurement you are now conducting...

To calculate the confidence interval around the mean of a set of N replicate measurements, it can be shown that the confidence intervals become smaller by a factor of $1/N^{1/2}$, so in this case the confidence limit for the true mean is

$$\mu = \bar{x} \pm \frac{z(P)\sigma}{\sqrt{N}}.$$

Your choice of z determines your confidence level.

If the number of individual values in a sample is small, say < 20 , and/or it is uncertain how well s represents σ , a value for the t -statistic from Student's t -table should be used in place of z :

$$\mu = \bar{x} \pm \frac{t(N-1 \text{ degrees of freedom [df] and at probability } P)\sigma}{\sqrt{N}}.$$

Student's t-Table

df	80%	90%	95%	99%	df	80%	90%	95%	99%
1	3.078	6.314	12.706	63.657	16	1.337	1.746	2.120	2.921
2	1.886	2.920	4.303	9.925	17	1.333	1.740	2.110	2.898
3	1.638	2.353	3.182	5.841	18	1.330	1.734	2.101	2.878
4	1.533	2.132	2.776	4.604	19	1.328	1.729	2.093	2.861
5	1.476	2.015	2.571	4.032	20	1.325	1.725	2.086	2.845
6	1.440	1.943	2.447	3.707	21	1.323	1.721	2.080	2.831
7	1.415	1.895	2.365	3.500	22	1.321	1.717	2.074	2.819
8	1.397	1.860	2.306	3.355	23	1.319	1.714	2.069	2.807
9	1.383	1.833	2.262	3.250	24	1.318	1.711	2.064	2.797
10	1.372	1.812	2.228	3.169	25	1.316	1.708	2.060	2.787
11	1.363	1.796	2.201	3.106	26	1.315	1.706	2.056	2.779
12	1.356	1.782	2.179	3.055	27	1.314	1.703	2.052	2.771
13	1.350	1.771	2.160	3.012	28	1.313	1.701	2.048	2.763
14	1.345	1.761	2.145	2.977	29	1.311	1.699	2.045	2.756
15	1.341	1.753	2.131	2.947	30	1.310	1.697	2.042	2.750

df	80%	90%	95%	99%
infinity	1.282	1.645	1.96	2.576

Note $t(df,P)$ increases as sample size decreases and as confidence level increases – as we would expect.

Compare the $t(\infty,P)$ values with $z...$ there the same! As $N \rightarrow \infty$, the sample size become the entire population and $z(P) = t(\infty,P)$

example: M&Ms

Rules for Rejection of Data Points

Sometimes a data point in a set of replicate measurements just seems to be an outlier. Should we keep it and calculate the mean, running the risk that we will unfairly bias our mean by including a “bad” data point that maybe was a mistake (incorrect reading, improper sample preparation...)? Or should we eliminate it, running the risk that we eliminate a correctly recorded data point?

The accepted test is the *Q test*. For this, we calculate the difference between the suspect result and the closest result, and divide that by the spread of the entire set (including the suspect point). The resulting ratio *Q* is compared with critical *Q* values that are cutoffs for various confidence intervals. If *Q* is greater than the cutoff, the data point can be rejected with the corresponding level of confidence.

Number of Observations	Reject if $Q > Q_{crit}$		
	Q_{crit} 90% confidence rejection cutoff	Q_{crit} 96% confidence rejection cutoff	Q_{crit} 99% confidence rejection cutoff
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
10	0.41	0.48	0.57

Example

In the data set (55.95, 56.00, 56.04, 56.08, 56.23), can the “suspect” result 56.23 be rejected?

The nearest value is 56.08, and the full spread is $56.23 - 55.95 = 0.28$

$$Q = \frac{56.23 - 56.08}{56.23 - 55.95} = 0.54$$

Since we have five measurements, the table above tells us we cannot reject it with 90% confidence ($Q_{crit} = 0.56$).

So, we see that *Q* expresses the fraction of the total spread of the data that can be accounted for by the suspected outlier.

Comparison of Two Experimental Means

Usually when we run experiments, we change conditions and see how the system responds. We should always ask, when the mean measured under condition 1 differs from the mean measured under condition 2, is the difference in the means *statistically significant*?

The true mean of the N_1 measurements conducted under condition 1 will be

$$\mu_1 = \bar{x}_1 \pm \frac{t(\text{df} = N_1 - 1, P)s}{\sqrt{N_1}}$$

and for the N_2 measurements conducted under condition 2, we have

$$\mu_2 = \bar{x}_2 \pm \frac{t(\text{df} = N_2 - 1, P)s}{\sqrt{N_2}}$$

where t is again the Student's t -value, a factor that is chosen based on the confidence level we choose when making our comparison. ("Student" = Gosset, a Guinness brewery statistician forced to publish under a pseudonym)

This is also tabulated:

For determining whether a difference is statistically significant:

$N_1 + N_2 - 2$	t factor for confidence interval		
	90%	95%	99%
1	6.31	12.7	63.7
2	2.92	4.30	9.92
3	2.35	3.18	5.84
4	2.13	2.78	4.60
5	2.02	2.57	4.03
6	1.94	2.45	3.71
7	1.90	2.36	3.50
8	1.86	2.31	3.36
9	1.83	2.26	3.25
10	1.81	2.23	3.17
11	1.80	2.20	3.11
12	1.78	2.18	3.06
13	1.77	2.16	3.01
14	1.76	2.14	2.98
∞	1.64	1.96	2.58

To establish whether or not the two measured means are really different, we propose the *null hypothesis*, in other words, we propose that they are *not* really different, and we try to reject that null hypothesis.

For a given confidence level (a given value of t), if \bar{x}_1 and \bar{x}_2 really are identical, the difference $\bar{x}_1 - \bar{x}_2$ should be within

$$\bar{x}_1 - \bar{x}_2 = \pm t(\text{df} = N_1 + N_2 - 2, P) s / \sqrt{\frac{N_1 N_2}{N_1 + N_2}} = \pm t(\text{df} = N_1 + N_2 - 2, P) s \sqrt{\frac{N_1 + N_2}{N_1 N_2}}$$

If the experimental difference $\bar{x}_1 - \bar{x}_2$ is greater than the term on the right hand side, then we reject the null hypothesis. In other words, we say that \bar{x}_1 and \bar{x}_2 really are different.

Example: Six analyses of a barrel of wine yielded a mean alcohol content of 12.61%. Four analyses of a second barrel yielded a mean alcohol content of 12.53%. The standard deviation of all ten analyses was 0.070%. Is there a difference between the two barrels?

$$\bar{x}_1 - \bar{x}_2 = 12.61 - 12.53 = 0.08$$

If we choose a 95% confidence level, for $N_1 + N_2 - 2 = 6 + 4 - 2 = 8$, then the table above gives $t = 2.31$. Calculate

$$t(8, 95\%) s \sqrt{\frac{N_1 + N_2}{N_1 N_2}} = (2.31)(0.070) \sqrt{\frac{6 + 4}{(6)(4)}} = 0.10$$

Since the difference $\bar{x}_1 - \bar{x}_2 = 0.08$ is less than 0.10, then we cannot say that the barrels are really different.

Propagating Precision/Error Estimates

What to do when multiple measurements with associated errors are used to compute a result in an equation?

e.g. $w = f(x, y, z, \dots)$ with data for x, y and z

Two scenarios:

1. Data for different parameters are linked – i.e. each member of a sample has all measurements needed for a calculation performed on it. In this case, compute a result for each set of measurements, average the final results and compute the confidence limits that correspond to this final average.

In this case $\bar{w} = \bar{f}(x, y, z, \dots)$ and

$$\text{confidence limits} = \frac{t(\text{df} = (N_{(x,y,z)} - 1); P) * s(w)}{\sqrt{N_{(x,y,z,\dots)}}}$$

2. Data for different parameters are independent – i.e. some members of a sample have one measurement performed, other members of a sample have a second type of measurement performed, etc. In this case, compute averages and confidence limits for each measurement separately. Then use the averaged measurements to compute the final average result. Next, use propagation of error formula to find the standard deviation (or variance) of the final result from the individual measurement standard deviations (or variances). Finally, compute the confidence limits for the final result.

In this case $\bar{w} = f(\bar{x}, \bar{y}, \bar{z}, \dots)$ and

$$\text{confidence limits} = \frac{t(\text{df} = (N_x - 1) + (N_y - 1) + (N_z - 1) + \dots; P) * s(w)}{\sqrt{\frac{N_x N_y N_z \dots}{(N_x + N_y + N_z + \dots)}}}$$

where if the errors comprising the standard deviations (variances) of each of the individual parameters in an equation are normally distributed, can estimate the standard deviation (variance) of calculated result using

$$s^2(w) = \left(\frac{\partial f}{\partial x}\right)_{\bar{x}, \bar{y}, \bar{z}, \dots}^2 s^2(x) + \left(\frac{\partial f}{\partial y}\right)_{\bar{x}, \bar{y}, \bar{z}, \dots}^2 s^2(y) + \left(\frac{\partial f}{\partial z}\right)_{\bar{x}, \bar{y}, \bar{z}, \dots}^2 s^2(z) + \dots$$

Here $\partial f / \partial x$ represents the partial derivative of f w.r.t. x . So, take the derivative of f w.r.t. x , treating other the variables (e.g. y, z, \dots) as constants

example

Suppose we wanted to estimate the density of a bone tissue scaffold created by LOM – laminated object manufacturing – e.g. Lone Peak Engineering’s MedLAM process – build up an object layer by layer using ceramic tape, with each layer cut by a laser, then burn out the binder and sinter the ceramic particles to make a solid. Can use slices of an MRI image to determine where cuts in each layer should be made.

e.g. see <http://www.javelin3d.com/pdf/awards/BioceramicRP.pdf>

Use the density measurement to estimate the porosity of the implant – optimize porosity to maximize bone tissue in-growth

Suppose 6 ceramic (alumina) scaphoid (wrist bone) replacements are fabricated using an LOM technology such as the MedLAM process. Estimate the average density of the ceramic scaphoids and report with 95% confidence limits. Determine the porosity of the ceramic scaphoids.

The density of alumina is 3.98 g/cm^3 .

Scenario #1

scaphoid	mass (“x”) (g)	volume (“y”) (mL)	density (“w”) = mass/volume (g/mL)
A	31.22	11.3	
B	32.17	11.47	
C	33.38	11.56	
D	29.95	10.99	
E	30.5	11.11	
F	29.72	10.79	

Scenario #2 scaphoid	mass (“x”) (g)	volume (“y”) (mL)	density (“w”) = mass/volume (g/mL)
A	31.22		
B	32.17		
C	33.38		
D		10.99	
E		11.11	
F		10.79	

“Figures often beguile me, particularly when I have the arranging of them myself; in which case the remark attributed to Disraeli would often apply with justice and force: ‘There are three kinds of lies: lies, damned lies and statistics.’” -Mark Twain