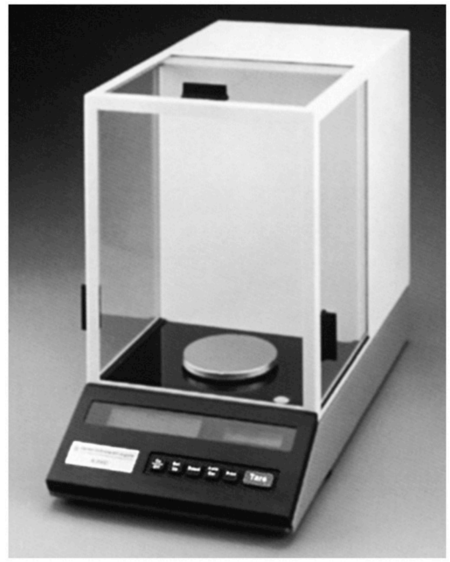
Why Aren't Values from Analyses Exact?

Exactly 12 eggs, no uncertainty



Some associated uncertainty

Systematic and Random Errors
Both sources of experimental error (Uncertainty)

• **Systematic Errors** - determinate, reproducible
- Due to poor technique, faulty calibration, poor design
- Uncalibrated volumetric or balance
- Not correcting for air buoyancy of liquid
- Side reaction in a titration
- Difficult to correct for with statistics but calibration with standards may find the error so that it can be corrected
- Controls the accuracy of measurement

• **Random Error** - indeterminate, non-reproducible
- Small errors are more frequent than large errors
- Errors are distributed about a mean value
- Easily treated with statistical methods (Gaussian Stats)
- Controls the precision of measurement

How Do We Determine Uncertainty?

Mean and Standard Deviation (x ± Δx)

Average or mean value: $\bar{x} = \dfrac{x_1 + x_2 + x_3 + ..x_n}{n}$

- This is the most useful method to report replicate measurements when the variations are small and randomly distributed (NO SYSTEMATIC ERROR).

• **Standard deviation (s):** describes the degree of scatter in the data set.
- Useful when the scatter is random; estimates the absolute error in same units
- The stdev is used along with the mean to report the value and its error

x ± s in g, mmol, wt %, etc

$$s = \sqrt{\frac{\left(x_1 - \bar{x}\right)^2 + \left(x_2 - \bar{x}\right)^2 + \left(x_3 - \bar{x}\right)^2 + ..\left(x_n - \bar{x}\right)^2}{n-1}}$$

•**Relative sd (rsd):** dimensionless value - rsd $= \frac{s}{\bar{x}}$

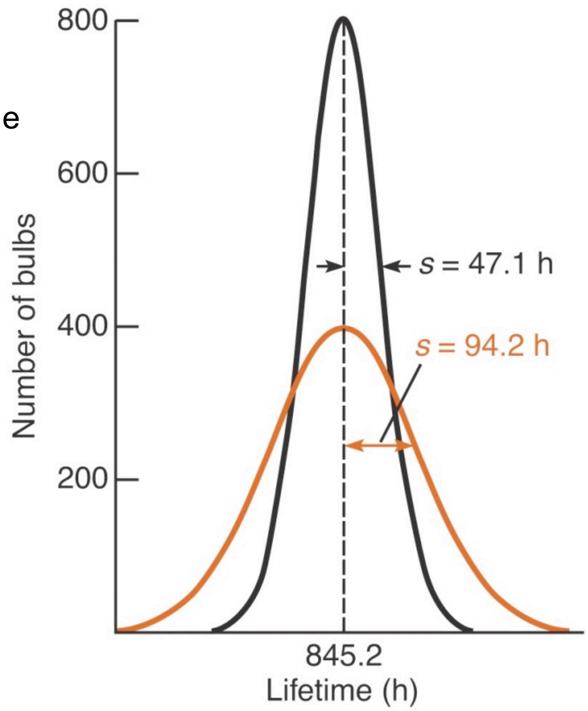
- Expressed as %, ppt, ppm, etc
(XX g, mmol, wt %, etc.) ± (rsd in %, ppt)

Examples:
Data: 1.012, 1.007, 1.022, 1.020, 1.017, 1.014 g
Mean = 6.092/6 = 1.015 and s = 0.0055; rsd = 0.0055/1.015 = 0.5%
We report 1.015 ± 0.006 g or 1.015 g ± 0.5%

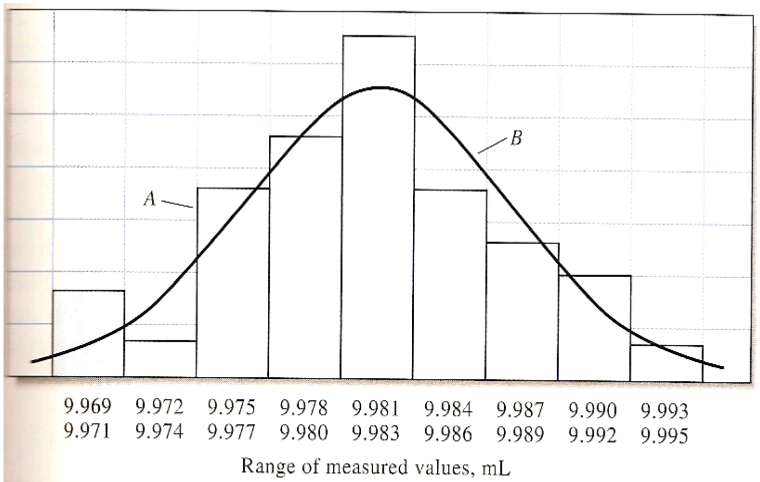
Normal Distribution -The Gaussian Curve

Statistical analysis is based on the assumption that random errors in analytical results follow a Gaussian, or normal distribution.

Gaussian Distribution:
• Mean is peak in distribution
• Large deviations from the mean are less probable than small deviations
• 1σ = ~ 68.3%
• 2σ = ~ 95.5%
• 3σ = ~ 99.7%



Distribution of the 50 results of 10 mL pipet calibration and corresponding Gaussian curve with a mean value and standard deviation:



Sources of uncertainties in the calibration of a pipet include:
(1) visual judgment (water level, mercury level in the thermometer);
(2) variations in the drainage time and in the angle of the pipet as it drains;
(3) temperature fluctuations, which affect the volume of the pipet, the viscosity of the liquid, and the performance of the balance;
(4) vibrations and drafts that cause small variations in the balance readings. And many other sources of random uncertainty.

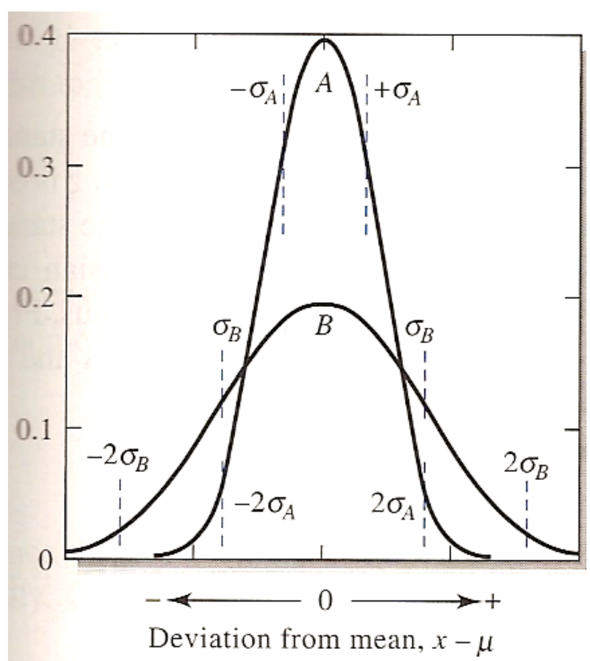
The Gaussian Curve

When the area of the curve is normalized to 1, it is described by:

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{-(x-\mu)^2}{2\sigma^2}}$$

y is the probability of observing a value x
μ - population mean or true value
σ - population standard deviation or true standard deviation

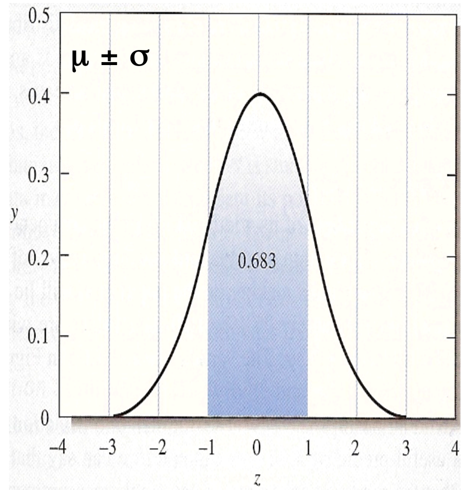
The smaller σ is, the narrower is the distribution of observed values.

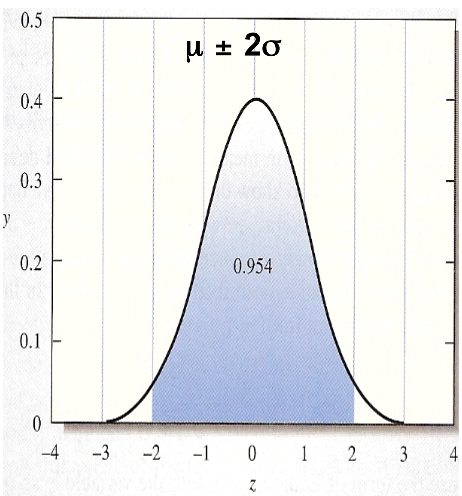


Gaussian Probabilities

Suppose we make a single measurement of x, and know σ from previous evaluation of the analytical method, then we can say:

For x to be in the range of true value μ	The probability is
$\mu \pm \sigma$	68.3 %
$\mu \pm 2\sigma$	95.5 %
$\mu \pm 3\sigma$	99.7 %





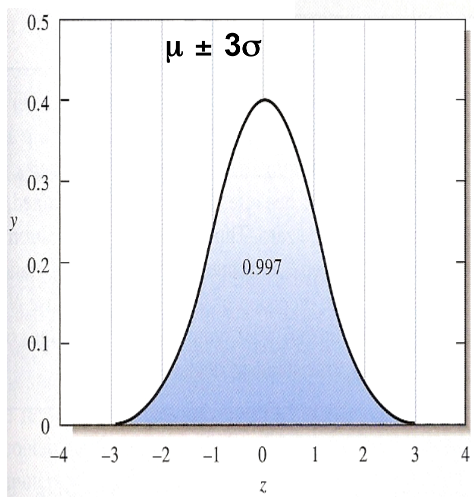


Table 4–1 Ordinate and area for the normal (Gaussian) error curve,

$$y = \frac{1}{\sqrt{2\pi}} e^{-z^2/2}$$

0z0[a]	y	Area[b]	0z0	y	Area	0z0	y	Area
0.0	0.398 9	0.000 0	1.4	0.149 7	0.419 2	2.8	0.007 9	0.497 4
0.1	0.397 0	0.039 8	1.5	0.129 5	0.433 2	2.9	0.006 0	0.498 1
0.2	0.391 0	0.079 3	1.6	0.110 9	0.445 2	3.0	0.004 4	0.498 650
0.3	0.381 4	0.117 9	1.7	0.094 1	0.455 4	3.1	0.003 3	0.499 032
0.4	0.368 3	0.155 4	1.8	0.079 0	0.464 1	3.2	0.002 4	0.499 313
0.5	0.352 1	0.191 5	1.9	0.065 6	0.471 3	3.3	0.001 7	0.499 517
0.6	0.333 2	0.225 8	2.0	0.054 0	0.477 3	3.4	0.001 2	0.499 663
0.7	0.312 3	0.258 0	2.1	0.044 0	0.482 1	3.5	0.000 9	0.499 767
0.8	0.289 7	0.288 1	2.2	0.035 5	0.486 1	3.6	0.000 6	0.499 841
0.9	0.266 1	0.315 9	2.3	0.028 3	0.489 3	3.7	0.000 4	0.499 904
1.0	0.242 0	0.341 3	2.4	0.022 4	0.491 8	3.8	0.000 3	0.499 928
1.1	0.217 9	0.364 3	2.5	0.017 5	0.493 8	3.9	0.000 2	0.499 952
1.2	0.194 2	0.384 9	2.6	0.013 6	0.495 3	4.0	0.000 1	0.499 968
1.3	0.171 4	0.403 2	2.7	0.010 4	0.496 5	∞	0	0.5

a. $z = (x - \mu)/\sigma$

b. The area refers to the area between z = 0 and z = the value in the table. Thus the area from z = 0 to z = 1.4 is 0.419 2. The area from z = −0.7 to z = 0 is the same as from z = 0 to z = 0.7. The area from z = −0.5 to z = +0.3 is (0.191 + 50.117 9) = 0.309 4. The total area between z = −∞ and z = +∞ is unity.

Table 4-1
Quantitative Chemical Analysis, Seventh Edition

If we have a group of numbers normally distributed about the mean then:

1) Are large deviations from the mean probable?

2) What percent are between 0 and +σ from the mean? 0 and 2σ from the mean? What percent are between 1σ and 2σ?

3) If we pick a number at random, where is it most likely from on the distribution?

Example From Book

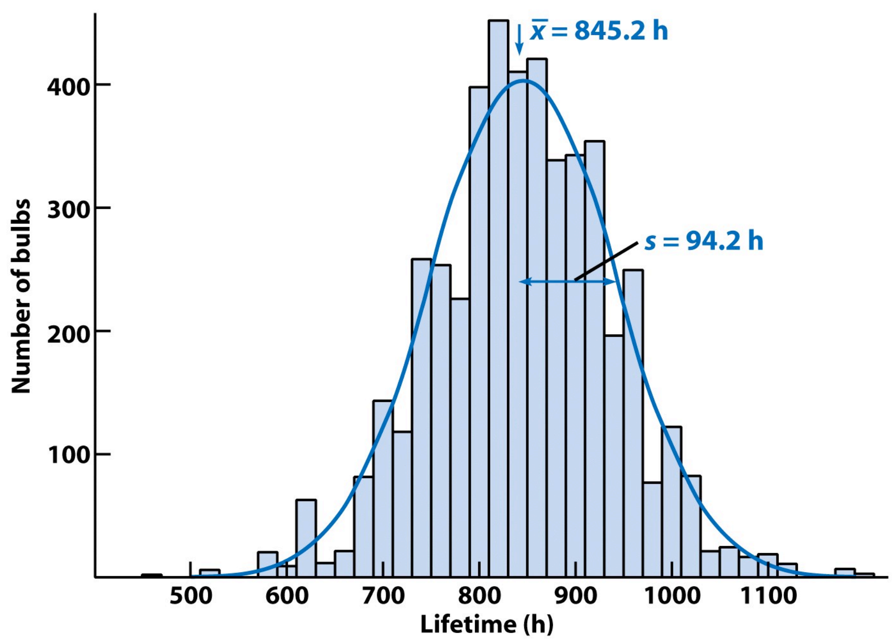


Figure 4-1
Quantitative Chemical Analysis, Seventh Edition

How many light bulbs have a lifetime less than 600 h?

1) Calculate z ; # std. dev. away from mean.
2) Find value on table.
3) Take difference

The Confidence Interval

So far, no distinction between $\bar{x}$ and μ, and s & σ, has been made. As n increases $\bar{x}$ approaches μ, but in the lab n~5 or so. How do we say anything about μ?

We use Confidence Interval (CI). We can say μ lies within a certain range about $\bar{x}$ with a certain "confidence".

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}} \quad \text{or} \quad \mu - \bar{x} = \pm \frac{ts}{\sqrt{n}}$$

where $\bar{x}$ is the observed mean and s is the observed sd,
n is the number of observations
t is Student's t for n-1 degrees of freedom (a tabulated value)

The Student's t-table

Table 4-2 **Values of Student's *t***

	Confidence level (%)						
Degrees of freedom	**50**	**90**	**95**	**98**	**99**	**99.5**	**99.9**
1	1.000	6.314	12.706	31.821	63.657	127.32	636.619
2	0.816	2.920	4.303	6.965	9.925	14.089	31.598
3	0.765	2.353	3.182	4.541	5.841	7.453	12.924
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959
7	0.711	1.895	2.365	2.998	3.500	4.029	5.408
8	0.706	1.860	2.306	2.896	3.355	3.832	5.041
9	0.703	1.833	2.262	2.821	3.250	3.690	4.781
10	0.700	1.812	2.228	2.764	3.169	3.581	4.587
15	0.691	1.753	2.131	2.602	2.947	3.252	4.073
20	0.687	1.725	2.086	2.528	2.845	3.153	3.850
25	0.684	1.708	2.060	2.485	2.787	3.078	3.725
30	0.683	1.697	2.042	2.457	2.750	3.030	3.646
40	0.681	1.684	2.021	2.423	2.704	2.971	3.551
60	0.679	1.671	2.000	2.390	2.660	2.915	3.460
120	0.677	1.658	1.980	2.358	2.617	2.860	3.373
∞	0.674	1.645	1.960	2.326	2.576	2.807	3.291

NOTE: In calculating confidence intervals, σ may be substituted for s in Equation 4-6 if you have a great deal of experience with a particular method and have therefore determined its "true" population standard deviation. If σ is used instead of s, the value of t to use in Equation 4-6 comes from the bottom row of Table 4-2.

(Degree of freedom is often determined by n-1)
• As confidence level increases, so does t
• As d.o.f. goes up, t goes down

Example from Book

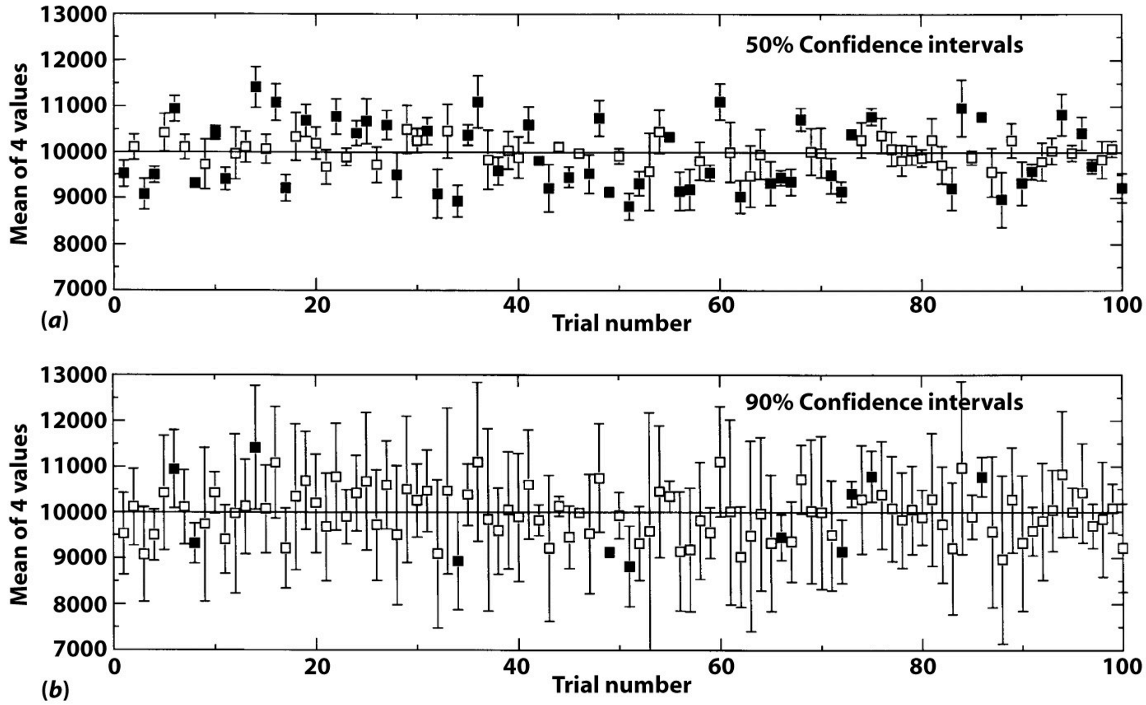


Figure 4-5
Quantitative Chemical Analysis, Seventh Edition

Each value of the mean with the associated confidence interval either includes or excludes the true mean. The CI defines the percentage of times the true mean is within the CI.

At a given confidence level, e.g., 90 %, how can we reduce the confidence intervals?

What does a 99.9% CI mean? Is that useful?

Calculating the Confidence Interval

Results for wt % glucose in a sample:
71.21 71.41 70.90 71.32 wt. % give $\bar{x}$ = 71.21 and s = 0.22
or 71.2 ± 0.2 wt %.

At the 95% confidence level, the confidence interval is

$$\mu - \bar{x} = \pm \frac{ts}{\sqrt{n}} = \pm 3.2 \times 0.22/\sqrt{4} = \pm 0.352 = \pm 0.3_5 \qquad \text{(DOF = n-1 = 3)}$$

or $\mu = 71.2_1 \pm 0.3_5$

So, there is a 95% chance that the true mean, m, lies within the range $71.2_1 \pm 0.3_5$ or from 71.5_6 to 70.8_6.

Comparison of Means (Sec. 4-3)

•Suppose we have several mean values for an unknown

- –We measured a mean on two different days
- –We measured a mean with two different methods
- –We measured a mean and want to compare it to the results from another lab
- –We are testing the null hypothesis, that the means are the same

•Why would these cases arise?

- –It took several days to make all the measurements
- –We are trying to validate our measurement method
  - •Comparing inter-lab variation to test for accuracy of everyone's results
  - •Comparing with well known standard values to check our accuracy

Comparison of a Mean to a Standard

Case 1. (by text definition, Sec. 4-3): Compare measured mean (n replicates) against a known standard value.

e.g., one would do this to standardize a method using a well known standard sample.

How?

Compare t_{calc} to t_{tab} to determine if the values are the same or different.

$$t_{calc} = \frac{|\mu - \bar{x}|}{s}\sqrt{n}$$

Then obtain t_{tab} from a t-table for the desired level of confidence, usually 95%, and for the number of degrees of freedom, given by d.o.f. = n-1.

If $t_{calc} > t_{tab}$ then the values are different from each other within the confidence limit selected. We conclude there is some form of systematic error present in experimental value.

If $t_{calc} < t_{tab}$ then the values are the same within the chosen confidence limit.

Example.

Again back to the glucose example, if we know the true value of the sample (i.e., the analyzed sample is a standard sample with a known % value) is 71.50%, we can determine whether our measured value agrees with the true value within experimental error at the 95% confidence level.

Results for wt % glucose in a sample:

71.21 71.41 70.90 71.32 wt. % give $\bar{x}$ = 71.21 and s = 0.22
or 71.2 ± 0.2 wt %.

$t_{calc.}$ = | 71.21-71.50| / 0.22 × √4
= 2.636

t_{tab} = 3.182 (95% confidence and 3 d.o.f.)

Since $t_{calc} < t_{tab}$, we can conclude that our measured value agrees with the true value within experimental error at the 95% confidence level.

Alternatively...

$$\mu - \bar{x} = \frac{ts}{\sqrt{n}}$$

s = std. dev.

t = the value for the desired CI and d.o.f.

If the left is greater than the right, reject the null, the values are different.

Comparing Two Measured Means

Case 2. (text definition): to determine whether two sets of replicate measurements give the same or different results, within a stated confidence level.

We calculate t according to:

$$t_{calc} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{pooled}}\sqrt{\frac{n_1 n_2}{n_1 + n_2}} \qquad s_{pooled} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$$

where:

n_1 is number of measurements of x_1 by method 1, with an observed sd of s_1.

n_2 is number of measurements of x_2 by method 2 with an observed sd of s_2.

s_{pooled} is the pooled sd for the confidence interval

If $t_{(calc)} > t_{(table)}$ for $(n_1 + n_2 - 2)$ degrees of freedom, the two results differ at the confidence level selected for comparison.

Alternatively...

$$|\bar{x}_1 - \bar{x}_2| = \frac{t s_p}{\sqrt{\frac{n_1 n_2}{n_1 + n_2}}}$$

- s_p= pooled std. dev.
- t is the value for the desired CI and d.o.f.
- If the left is greater than the right, reject the null, the values are different.

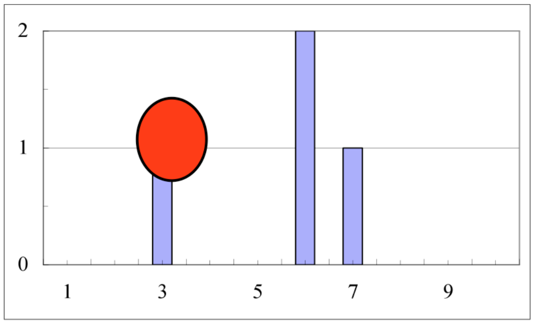
F Test (Sec. 4-4)
To test if two standard deviations are statistically similar.

$$F_{calc} = \frac{s_1^2}{s_2^2}$$

- Put the larger s on top such that $F_{calc} \geq 1$
- If $F_{calc} < F_{table}$ then use std equations
- If $F_{calc} > F_{table}$ then use modified equations

Example (from Text): Is the standard deviation from chemical decomposition significantly greater than the standard deviation from air in Rayleigh's Data?

Are Outliers Skewing Your Results?



- In a small data set, some point may seem suspiciously far from the other data points
  - You suspect determinate error but do not know of any

- You can
  - Repeat the measurement (best choice)
  - Use the median value
  - Apply the G-test to retain or discard the suspect data point

- You must
  - Use the G-test only once on a set of measurements of a sample
  - Reject a value on the basis of the G-test only if reporting the mean, and do not reject it if reporting the median

Other Statistics:

Median value: middle value of a data set arranged sequentially, including duplicates.
- Average of two middle values if there are an even number of points
- Median is useful if there is large scatter in a small data set, as it reduces the effect of outlying points.

>> Use if one or more data points differ a lot from the central values.

Range: the difference between the highest and lowest point in the data set.
- Range is used when reporting the median.