CHEG237W Chemical Engineering Lab

Part I-1. Lab Overview and Safety
Part I-2. How to Write a Good Lab Report
Part II-1. Data Treatment and Statistics
Part II-2. Analysis of Kinetics Data
Part II-1. Data Treatment and Statistics
Why do we need Statistics?
• All physical processes are subject to random disturbances.
• STATISTICS provides a mathematical method of dealing with uncertainty in measurement, design, problem solving and decision-making processes.

How will statistics be helpful in Chemical Engineering Laboratory?
• Designing experiments and determining sample size (not covered here)
• Estimating precision of data
• Determining confidence intervals of calculated mean values
• Hypothesis testing (e.g. comparing 2 or more calculated means)
• Developing empirical models (regression analysis)
• Testing existing models (correlation analysis)

Conclusions drawn from your experiments must be backed by sound statistical arguments!
Definitions

Precision, Bias, Accuracy, Measures of Precision, Propagation of Error

PRIOR TO DATA ACQUISITION ONE SHOULD CONSIDER:
1. The accuracy and/or precision required in your data and calculations should be consistent with the projected use of the result.
2. It is desirable to complete the investigation and obtain the required accuracy and/or precision with a minimum of time and expense.

TYPICAL QUESTIONS TO ASK:
1. What types of errors are likely to enter a given measurement or calculation?
   2. To what extent do the errors in data influence the error in a result calculated from the data? (propagation of error)
2. What accuracy and/or precision is it economically feasible to obtain?
3. Is absolute accuracy and/or precision needed, or merely trends or differences?
Types of Uncertainty

1. Random or Indeterminate Errors
   The word “Precision” is used to describe random error. Precision is best quantified by the sample variance ($S^2$) or sample standard deviation ($S$) of values obtained by repeating trials several times.

Example:

n (=5) repeated trials from the draining tank experiment yield the data:

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Drain time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
</tr>
</tbody>
</table>

Sample mean or average = $x_m = \frac{1}{n} (x_1 + x_2 + ...)$  
Eqn. 1

Sample mean = $\frac{1}{5} (25 + 27 + 24 + 25 + 30) = 26.2$ s

Sample standard deviation = $S = \left[\frac{1}{n-1} \left\{ (x_1 - x_m)^2 + (x_2 - x_m)^2 + ... \right\} \right]^{1/2}$  
Eqn. 2

Sample standard deviation = $S = \left[\frac{1}{4} \left\{ (25-26.2)^2 + (27-26.2)^2 + (24-26.2)^2 + (25-26.2)^2 + (30-26.2)^2 \right\} \right]^{1/2} = 2.4$ s
Bias

2. Fixed or Systematic Errors

A consistent or repeated error. Systematic error is called “Bias”. Bias is determined by comparing the sample mean to the “reference” value of the measured property. Reference values can be (a) real, though unknown “true” values; (b) assigned values, arrived at by agreement among experts; or (c) the result of a hypothetical experiment which is approximated by a sequence of actual experiments. Only type (b) reference values render mathematical description of bias (bias = sample mean – assigned value). Total Accuracy is total absence of bias.

STATISTICS deals only with precision, not with bias (i.e. accuracy). Possible reasons for Poor Precision – fluctuations in surroundings, fluctuations in system, sloppy sampling or recording by a human, data taken by different people, fluctuations in measuring device, magnitude of the measured value, etc.…. Possible reasons for Bias – improper calibration of measuring device, malfunction in measuring device, consistent human error in sampling or measuring, etc….
Comparison
Standard Deviation and Confidence Intervals

**Precision:** in the measurement of dependent and independent variables can only be assessed if replicate measurements are made at a single experimental “condition”

Precision can be reported many different ways:

1) **Standard Deviation**
   How far, on average, replicate observations are from their mean:
   
   \[
   \text{Coeff of variation} = \left( \frac{\text{std dev}}{\text{mean}} \right) \times 100
   \]

2) **Confidence Intervals**
   A confidence interval = range of values between which the population mean can be expected to lie with a given certainty... they provide a probability statement about the likelihood of correctness.

   The two-sided 95% Confidence Interval (based on the Student-t distribution) is given by:

   \[
   x_m - t_{0.025} \frac{S}{\sqrt{n}} < \mu < x_m + t_{0.025} \frac{S}{\sqrt{n}}
   \]

   Eqn. 3
Example

CHEG 237W - Excel calculation of sample statistics and confidence intervals

Draining Tank Experiment – Replicate Data for drain time of water from a tank
Run 1 - pipe length = 10", diameter = 0.25"
Trial #  Time (s) Required to Drain 6” of fluid
1 25
2 27
3 24
4 25
5 30
sample size 5
Average 26.2, Excel command for Average = Average(list of numbers)
Stand Dev 2.4, Excel command for stand dev = STDEV(list of numbers)
95% Confidence Interval = 26.2 ± 2.1, Excel command for conf = Confidence(alpha, stdev, sample size)
Where alpha = (100-confidence level desired)/100...i.e. alpha=0.05 for 95% confidence

3) Error Bars.

In Excel, the value of error bars on data points can be based on 1) fixed values you define, 2) % of each data point, 3) specific number of std dev from the mean of the plotted values 4) std error of the plotted values 5) custom values you define.
Propagating Error

Propagating Error refers to uncertainty in a computed quantity \( u \) resulting from uncertainties in the primary measurements \( (x, y, z) \) on which it is based.

1. If \( u \) is a linear function of the primary measurements \( (x, y, z) \)
   i.e. \( u = ax + by + cz \) and \( x, y, \) and \( z \) are statistically independent measurements the variance in \( u \) is given by:

\[
\sigma^2(u) = \sigma^2(ax + by + cz) = a^2\sigma^2(x) + b^2\sigma^2(y) + c^2\sigma^2(z) \quad \text{Eqn. 4}
\]

2. If \( u \) is a non-linear function of the primary measurements, for example \( u = xyz \), and the measurements are statistically independent a method of linearization based on a Taylor expansion can be used. Suppose \( u = f(x, y, z) \)

\[
\sigma^2(u) = \left(\frac{\partial f}{\partial x}\right)^2 \sigma^2(x) + \left(\frac{\partial f}{\partial y}\right)^2 \sigma^2(y) + \left(\frac{\partial f}{\partial z}\right)^2 \sigma^2(z) \quad \text{Eqn. 5}
\]

Note- this method is valid when \( \sigma(x) \) is of the order of 10% \( x \) or smaller
Hypothesis Testing

**Hypothesis testing:** A formal procedure for determining “statistical significance” when comparing two methods, two operating conditions, two materials, etc. Hypothesis tests and confidence intervals are closely related. The procedure is:
1. Formulate hypotheses
2. Select appropriate distribution function for the test statistic
3. Specify the level of significance
4. Collect and analyze data and calculate an estimate of the test statistic
5. Define the region of rejection for the test statistic
6. Accept or reject hypotheses

**Hypotheses:** Statements that indicate the absence or presence of differences. Hypotheses consist of pairs of statements. The first hypothesis (null hypothesis) states that the sample means of two populations are equal:

The two means are equal: \( x_{m1} = x_{m2} \)

The second hypothesis (alternative hypothesis) can be stated various ways:
The two means are different: \( x_{m1} \neq x_{m2} \)
A Distribution function is a mathematical model describing the probability that a random variable X lies within the interval x1 to x2. The location, scale and shape of the function are usually characterized by one to three parameters (mean, variance, skewness). Uniform, normal, lognormal, student-t, and chi-squared are some examples of continuous distribution functions. The test statistic is the distribution function that you choose to represent your particular testing requirements. When comparing random samples drawn from two normally distributed populations, the student-t distribution is used:

Student-t test statistic:  \[ t = \frac{X_{m1} - X_{m2}}{S_p \left( \frac{1}{n_1} + \frac{1}{n_2} \right)^{0.5}} \]  \[ \text{Eqn. 6} \]

where \( S_p \) the pooled variance is given by

\[ S_p^2 = \frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2} \]  \[ \text{Eqn. 7} \]

\( S^2 \) is the sample variance, \( n \) is the sample size and the subscript 1 and 2 represent populations 1 and 2.
Hypothesis Testing

The level of significance ($\alpha$) represents the probability of rejecting the null hypothesis when indeed it is true. Selection of the level of significance should be based on an evaluation of the consequences of making an incorrect conclusion (in your case, a false conclusion is not life threatening…or is it?!) Typical values for $\alpha$ are 0.05 or 0.01.

The region of rejection consists of those values of the test statistic that would be unlikely if the null hypothesis were true. For a hypothesis test of two means, the region of rejection is a function of the degrees of freedom ($n_1+n_2-2$), level of significance ($\alpha$), and the statement of the alternative hypothesis:

If the alternative hypothesis is

- $X_{m1} \neq X_{m2}$
- $X_{m1} < X_{m2}$
- $X_{m1} > X_{m2}$

then reject the null hypothesis if

- $t < -t_{\alpha/2}$ or $t > t_{\alpha/2}$
- $t < -t_{\alpha}$
- $t > t_{\alpha}$

$t$ is the value calculated using Eqns. 6 & 7. $t_{\alpha}$ and $t_{\alpha/2}$ are found in the student-t table.

Accept or reject the null hypothesis by comparing the sample estimate of the $t$ statistic calculated using experimental data with tabulated values of $t_{\alpha}$ or $t_{\alpha/2}$. 
An Example

**CHEG 237W - Excel calculation of sample statistics and hypothesis testing**

**Draining Tank Experiment - Data for drain time of water from tanks with different length outlet pipes**

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Time (s)</th>
<th>Trial #</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td></td>
<td>Run 2</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>25</td>
<td>1</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>27</td>
<td>2</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
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<td>4</td>
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<td>4</td>
<td>37</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>5</td>
<td>36</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th>Run 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Size</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Average</td>
<td>26.2</td>
<td>35.80</td>
</tr>
<tr>
<td>Stand Dev</td>
<td>2.4</td>
<td>0.84</td>
</tr>
<tr>
<td>Confidence Interval =</td>
<td>$26.2 \pm 2.1$</td>
<td>$35.8 \pm 0.7$</td>
</tr>
</tbody>
</table>
An Example

Hypothesis Test of drain times from 1" and 10" length pipes

Null hypothesis = means of the two runs are equal
Alternative hypothesis = mean of the 10" pipe is less than mean of the 1" pipe

calculated $t = \frac{(20.2-35.8)/Sp}{(1/5+1/5)^{.5}}$

t = -8.48

where $Sp^2 = \frac{(5-1)(2.39)^2+(5-1)(.84)^2}{(5+5-2)}$

$Sp^2 = 3.2$

t department (for 5+5-2 degrees of freedom and level of significance $\alpha = 0.1$

t = 1.397

test = reject null hypothesis if $t < -t_{\alpha}$

-8.48 is less than -1.397 so we can be
90% certain that the null hypothesis is false!!!!
i.e. run 1 time is significantly different from run 2 time
## Table of Critical Values

<table>
<thead>
<tr>
<th>Degrees of freedom, ( k )</th>
<th>0.2500</th>
<th>0.1000</th>
<th>0.0500</th>
<th>0.0250</th>
<th>0.0100</th>
<th>0.0050</th>
<th>0.0025</th>
<th>0.0005</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1.000</td>
<td>3.078</td>
<td>6.314</td>
<td>12.706</td>
<td>31.821</td>
<td>63.657</td>
<td>127.321</td>
<td>536.627</td>
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<td>2.920</td>
<td>4.303</td>
<td>6.965</td>
<td>9.925</td>
<td>14.089</td>
<td>31.599</td>
</tr>
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<td>1.638</td>
<td>2.353</td>
<td>3.182</td>
<td>4.541</td>
<td>5.841</td>
<td>7.453</td>
<td>12.924</td>
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<tr>
<td>4</td>
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<td>1.533</td>
<td>2.132</td>
<td>2.776</td>
<td>3.747</td>
<td>4.604</td>
<td>5.598</td>
<td>8.610</td>
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<tr>
<td>5</td>
<td>0.727</td>
<td>1.476</td>
<td>2.015</td>
<td>2.571</td>
<td>3.365</td>
<td>4.032</td>
<td>4.773</td>
<td>6.869</td>
</tr>
<tr>
<td>6</td>
<td>0.718</td>
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<td>1.943</td>
<td>2.447</td>
<td>3.143</td>
<td>3.707</td>
<td>4.317</td>
<td>5.599</td>
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<td>1.415</td>
<td>1.895</td>
<td>2.365</td>
<td>2.998</td>
<td>3.499</td>
<td>4.029</td>
<td>5.048</td>
</tr>
<tr>
<td>8</td>
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<td>1.397</td>
<td>1.860</td>
<td>2.306</td>
<td>2.896</td>
<td>3.355</td>
<td>3.833</td>
<td>5.513</td>
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<td>9</td>
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<td>1.383</td>
<td>1.833</td>
<td>2.262</td>
<td>2.821</td>
<td>3.250</td>
<td>3.690</td>
<td>4.781</td>
</tr>
<tr>
<td>10</td>
<td>0.700</td>
<td>1.372</td>
<td>1.812</td>
<td>2.228</td>
<td>2.764</td>
<td>3.169</td>
<td>3.581</td>
<td>4.578</td>
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<td>11</td>
<td>0.697</td>
<td>1.363</td>
<td>1.796</td>
<td>2.201</td>
<td>2.718</td>
<td>3.106</td>
<td>3.497</td>
<td>4.347</td>
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<tr>
<td>12</td>
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<td>1.356</td>
<td>1.782</td>
<td>2.179</td>
<td>2.681</td>
<td>3.055</td>
<td>3.428</td>
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<td>1.771</td>
<td>2.160</td>
<td>2.650</td>
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<td>1.761</td>
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<td>15</td>
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<td>1.753</td>
<td>2.131</td>
<td>2.602</td>
<td>2.947</td>
<td>3.300</td>
<td>4.103</td>
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<td>16</td>
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<td>1.734</td>
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<td>2.878</td>
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<td>3.922</td>
</tr>
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<td>19</td>
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<td>1.328</td>
<td>1.729</td>
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<td>3.883</td>
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<td>1.725</td>
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<td>1.714</td>
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<td>2.807</td>
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<td>1.708</td>
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<td>1.706</td>
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<td>2.052</td>
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<td>2.704</td>
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<td>0.680</td>
<td>1.301</td>
<td>1.679</td>
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<td>2.412</td>
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<td>2.952</td>
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<td>50</td>
<td>0.679</td>
<td>1.299</td>
<td>1.676</td>
<td>2.009</td>
<td>2.403</td>
<td>2.678</td>
<td>2.937</td>
<td>3.496</td>
</tr>
</tbody>
</table>

**A-2. Critical Values for the Student-\( t \) Distribution (t_{\alpha,k})**

For Upper Tail Values
The One-Way ANOVA Test for \( k \) Population Means (Critical-Value Approach)

Assumptions
1. Independent samples
2. Normal populations
3. Equal population standard deviations

**Step 1** The null and alternative hypotheses are

\[ H_0: \mu_1 = \mu_2 = \cdots = \mu_k \]
\[ H_a: \text{Not all the means are equal.} \]

**Step 2** Decide on the significance level, \( \alpha \).

**Step 3** Obtain the three sums of squares, SST, SSTR, and SSE.

**Step 4** Construct a one-way ANOVA table to obtain the value of the \( F \)-statistic.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>SS</th>
<th>MS</th>
<th>( F )-statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment</td>
<td>( k-1 )</td>
<td>SSTR</td>
<td>SSTR ( k-1 )</td>
<td>( F = \frac{MSTR}{MSE} )</td>
</tr>
<tr>
<td>Error</td>
<td>( n-k )</td>
<td>SSE</td>
<td>SSE ( n-k )</td>
<td>[ F = \frac{SSTR}{SSE} ]</td>
</tr>
<tr>
<td>Total</td>
<td>( n-1 )</td>
<td>SST</td>
<td>SST</td>
<td>[ F = \frac{SSTR}{SSE} ]</td>
</tr>
</tbody>
</table>

**Step 5** The critical value is \( F_\alpha \) with df = \( (k-1, n-k) \), where \( n \) is the total number of observations. Use Table VIII to find the critical value.

**Step 6** If the value of the \( F \)-statistic falls in the rejection region, reject \( H_0 \); otherwise, do not reject \( H_0 \).

**Step 7** Interpret the results of the hypothesis test.
Data Regression: statistically deriving a mathematical relationship between a dependent variable and measured values of independent variables i.e. deriving an empirical model.

Linear regression using the “least-squares” criterion is an example of model development from experimental data.

Data Correlation: provides information about the strength and type of relationship between two or more variables or the strength of the relationship between observed values and predicted values, i.e. the degree to which one or more variables can be used to predict the values of another variable.

1) Coefficient of determination, $r^2$, is the (sum of the squared errors between the predicted value and the mean)/(sum of the squared errors between the observed value and the mean). It is the squared value of $r$, the correlation coefficient.

2) Hypothesis testing (performed on slope or $r$ or $r^2$)

3) Prediction intervals
Data Regression Examples

(1) Fitting a Line to Experimental Data
Example: calibrating a rotameter (rotameter reading vs flowrate)

(2) Fitting Curves to Experimental data (calculating polynomial coefficients and/or model parameters)
Example: developing an expression for the heat capacity of a gas as a function of temperature

(3) Estimating parameters in existing models from raw data
Example: finding Antoine constants \[ \log p = A + B/(T+C) \] from vapor pressure vs temperature data

(4) Comparing models derived from experimental data to existing models
Example: correlation of heat transfer data using dimensionless groups followed by comparison to existing empirical models

(5) Comparing the effects of various independent variables on the dependent variable
Example: comparing the effects of pipe diameter, pipe length, and viscosity on draining time