ChE 473A
Chemical Engineering Unit Operations
Laboratory Manual

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Preface

Any laboratory course involves careful planning, experimentation, data analysis, and some form of reporting the results. Chapters 2–4 of this manual are intended to give the necessary background information needed to perform each of these steps efficiently. Chapter 5 gives a quick overview of each of the operations which will be studied, suggests experiments which may be performed with each apparatus, and references which cover their behavior in greater detail. These operations include:

- distillation column,

- continuous flow reactors,

- gas membrane separation,

- gas-liquid absorption in a packed bed, and

- pumping performance.

Explicit functionality references are given for many numerical procedures implemented in Microsoft Excel 2007 (Microsoft Corp., Redmond, WA) and MATLAB (The MathWorks, Inc., Natick, MA). These programs are readily available to students at Washington University in St. Louis and are commonly employed for technical computing throughout industry and in academia. This should give the student a quantitative foundation in the analytical methods covered in this course.

Contents

Chapter 1

Introduction

Unit operations take raw materials and convert them into the desired product(s): heat, electricity, work, new chemical species, and species with improved purity. Understanding the fundamentals of unit operations is therefore essential for any chemical engineer and is what sets him or her apart from other engineers. Unfortunately, it is this broad area that also makes chemical engineering the most difficult engineering field. This text will attempt to distill the key ideas required to succeed in the unit ops lab. Each subsection of this text could comprise an entire semester of study and a corresponding textbook. Thus, the goal of the text is simply to give sufficient background for the purposes of this course. Additional references are included at the end of each chapter for the interested reader.

The first part of this text could be included in a manual for any laboratory course. It focuses on how to plan, analyze, and report experiments. The second part focuses on the specific unit operations which will be used in this course, suggests possible experiments, and gives sufficient background information to aid your understanding of the utility of these operations in chemical engineering practice.

Chapters 2–4 give a brief overview of the fundamentals of pre- and post-experimental preparation and analysis. Chapter 2 covers the selection of independent variable values used to map the dependent variable response, including statistical design of experiments for systems with multiple variables. Chapter 3 introduces statistical methods such as computing means, standard deviations, and conducting hypothesis testing using t-testing and analysis of variance (ANOVA). Chapter 4 details the various parts of a report or article.

Chapter 5 gives a brief overview of the five unit operations which will be studied in this course:

- batch distillation,

- continuous flow reactors,

- gas membrane separation,

- gas-liquid absorption with reaction in a packed bed, and

- pumping performance.

These operations utilize heat, mass, and momentum transfer between phases and process streams to develop useful products. The theoretical background on the operation of these operations forms the bulk of the chemical engineering literature. Therefore, its coverage in this text is limited to a cursory description of each process, accompanied by citations of literature which covers the operation in exhaustive detail, as well as some possible experiments.

Chapter 2

Planning Experiments

The key to successful experimentation is the deliberate selection of appropriate values of independent variables for testing. This selection requires a qualitative understanding of how the dependent (measured) variable $y(\vec{x})$ depends on the independent (controlled) variables $\vec{x} = \{x_1 \; x_2 \; ... \; x_n\}$. For example, if one expects *a priori* that $y(x)$ is a linear function of x, one may simply test linearly spaced values of x to generate representative correlations (Fig. 2.1A). However, if the response $y(x)$ was instead inversely proportional to x, a linear point spacing will not map the dynamic response well (Fig. 2.1B). Such a response is much more apparent if the dependent variables are selected according to a logarithmic spacing scheme and plotted on a logarithmic axis (Fig. 2.1C).

These examples should make it clear that careful selection of the test values for x before experimentation is essential to an accurate determination of the system response to a change in input.

Often, a system will have a sigmoidal response to a change in the independent variable (Fig. 2.2). The lower plateau is below the threshold, while the upper plateau is the saturation range. The rapidly rising intermediate section is the system's dynamic range. The slope of the response in this region is the system's sensitivity to changes in the independent variable. A good experimental plan will locate the threshold and saturation points and accurately characterize the dynamic range. An *a priori* understanding of the system's fundamentals is essential to selecting the test points.

2.1 Systems With Multiple Independent Variables

The above discussion describes typical system responses to a change in one independent variable while all other variables are held constant. Experimentation has historically been conducted in this manner because it is easy to understand the one-to-one relationship between the independent and dependent variable. This method is so ubiquitous that it has been given the name, "The Scientific Method," and is largely due to Thomas Edison, whose personal motto was that, "Genius is 1% inspiration, 99% perspiration." This method is also known as the "**One Factor At a Time**" (**OFAT**) method by statisticians.

Attempting to apply OFAT to a complex engineering system is problematic. Many independent variables usually exist, and the system's respones to changes in these variables
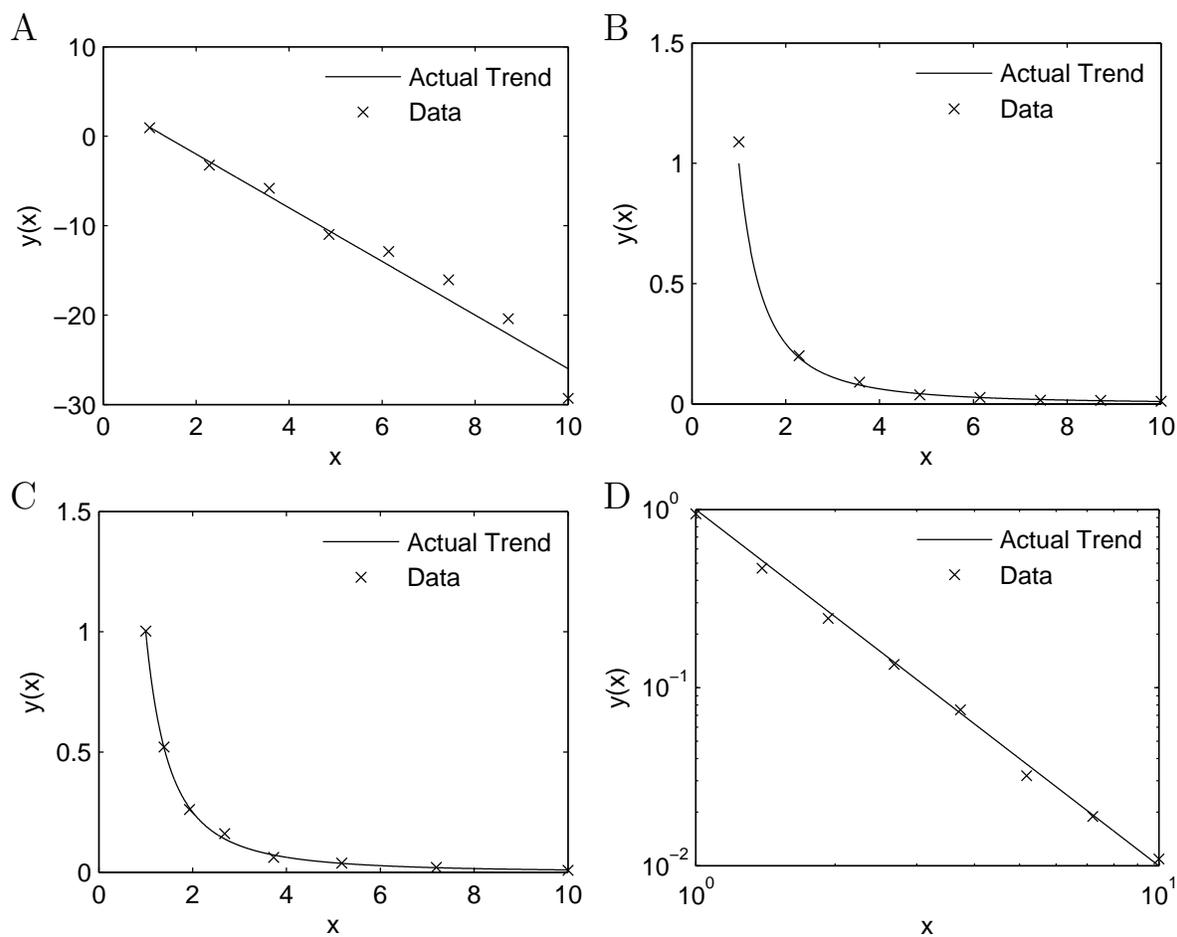
Figure 2.1: Sample figures showing the dependence of $y(x)$ on x. Linear point spacing maps the dynamic range well for a linear response (A), but not for an exponential response (B). Using logarithmically-spaced points (C) improves the number of observations within the dynamic range, while plotting on logarithmic axes (D) make the underlying trend in the data obvious.
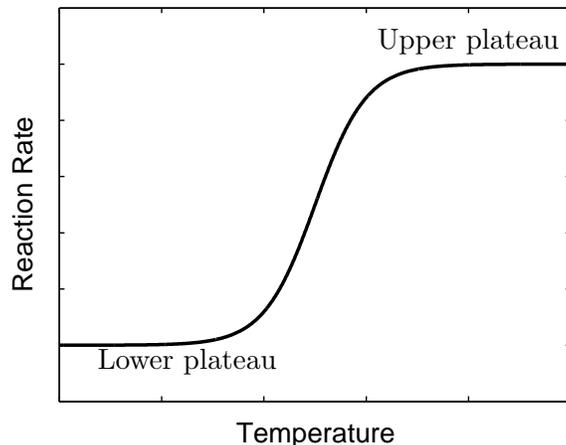
Figure 2.2: A sample sigmoidal response representing the effective reaction rate as a function of temperature. In a catalytic packed bed reactor, the lower plateau is a reaction-rate limited regime, whereas the rate at the upper plateau is diffusion-limited. Within the dynamic range, both diffusion and reaction rate are changing rapidly.

often involve interactions between one or more of the variables. Thus, changing x_1 while holding $x_2, x_3, ...x_n$ constant will yield information about the system response only at these fixed values. Once the optimal value for x_1 is found to be x_1^*, its value is held constant and x_2 is varied until its optimal value is found. This is repeated until optimal values of $\vec{x}$ have been located. This is not only tedious but also relies on the assumption that no interactions between independent variables exist. If any interactions exist, the final "optimal" configuration may be far from optimal. Perhaps this is why Edison famously said, "I have not failed 1,000 times. I have successfully discovered 1,000 ways that do not work, and I do not need to try them again."

Thankfully, there is a better way to find the optimal configuration for complex systems of many variables. Rather than using a serial method in which the system's response to variables are tested sequentially in isolation, a parallel testing method may be used to develop a "response surface," which describes the system's response to changes in multiple variables. While commercial software programs may design a response surface for up to 50 interactive effects, the number of experiments required for such an undertaking is prohibitive. Therefore, a more efficient approach is generally adopted where initial "screening" experiments are used to ascertain which variables play a significant role in determining system performance. Once these variables have been identified, a response surface method may be used to find the optimal configuration $\vec{x}^*$ Describing the details of such designs is beyond the scope of this text and are usually handled internally by an appropriate software program. This information is presented here to enable the interested reader to pursue further knowledge in this area by consulting the wealth of available literature on the subject of Design of Experiments (DOE) and RSM.

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2.1.1 Screening Designs

Screening designs generally assume linearity in the system's response to changes in $\vec{x}$. The system response $y(\vec{x})$ is measured at two extreme values for each x (labeled here as $x^{\pm}$), allowing an estimate of the linear effect of x. The values of x should correspond to the limits of the range which within which you expect the optimal configuration x^*. These limits may be determined based on preliminary experimentation, data from the literature, or experience. If it is known *a priori* that the response to x is nonlinear (e.g. one should anticipate that the density of a gas will vary as $1/T$ rather than linearly with T), then one may choose to define x in terms of the anticipated response (e.g. $x = 1/T$ may be used rather than $x = T$). Quadratic responses may be examined by adding an intermediate point for each x at the midpoint of the range of x, though this is not discussed further here.

While many types of screening designs exist, the most common are **factorial designs**. A **full factorial design** involves testing every combination $x_1^{\pm}x_2^{\pm}...x_n^{\pm}$, which requires 2^n experiments. This approach elucidates the effects of all linear effects and the first-order interactions of each of these parameters. However, the number of experiments required to achieve this resolution becomes very large very quickly as the number of factors increases, requiring 128 experiments when testing 7 factors.

Physical insight into the problem often allows one to decrease the required number of experiments by utilizing a **fractional factorial design**. Fractional designs decrease the number of experiments necessary to achieve a given resolution by testing only certain combinations of $x_1^{\pm}x_2^{\pm}...x_n^{\pm}$. Mathematicians have developed matrices describing such experiments which minimize the number of experiments required to achieve a given resolution. The downside to fractional designs is that some effects and interactions will be confounded, requiring a bit of thought during the selection and ordering of the parameters to avoid masking a main effect with an interaction which is likely to be significant. Thus, with a bit of thought, one may examine the most likely effects and interactions while conducting a much smaller number of experiments.

2.1.2 Response Surface Methods (RSM)

Once preliminary screening has revealed the significant effects, RSM may be utilized to find the optimal configuration $\vec{x}^*$ without the assumption of linearity. Near $\vec{x}^*$, the system's response is often highly nonlinear such that the effects estimated using the screening methods discussed above will result in significant errors. RSM again requires the selection of limits $x^{\pm}$. The RSM software will then specify the test points, order of experiments, and all of the other necessary details. Once the requisite experiments have been completed, the user simply enters the responses at each test point into the software. The software will perform a statistical analysis and report the most likely form of the response surface and its coefficients. The response surface will generally have the form

$$
\begin{aligned}
y(x_1,\ x_2,\ ...\ x_n) = c_0 + c_1 x_1 + c_2 x_2 + ...c_n x_n && \text{Linear terms} \\
+ c_{1,2}x_1 x_2 + c_{1,3}x_1 x_3 + ...c_{n-1,n} && \text{Interaction terms} \\
+ c_{1,1}x_1^2 + c_{2,2}x_2^2 + ...c_{n,n}^2 && \text{Quadratic terms} \\
+ ... && \text{Higher order terms}
\end{aligned}
\tag{2.1}
$$

which has the equivalent form

$$y(x_1, \ x_2, \ ... \ x_n) = \underbrace{c_0 + \sum_{i=1}^{n} c_i x_i +}_{\text{Linear}} \underbrace{\sum_{i=1}^{n}\sum_{j=1}^{n} c_{i,j} x_i x_j}_{\text{Interactions and Quadratic}} \quad +... \tag{2.2}$$

2.2   Summary

A bit of care in preparing an experimental design can dramatically decrease the required number of experiments needed to understand and optimize the behavior of a given unit operation. A detailed knowledge of the underlying mechanisms, driving forces, and resistances in the system, along with the methods presented here, will allow the engineer to improve or even optimize system performance.

2.3   Additional Reading

- http://www.statease.com/

- http://www.chemicalprocessing.com/articles/2006/166.html

Chapter 3

Data Reduction and Analysis

After an experiment is planned and carried out, the resulting data must be reduced and analyzed. Even if appropriate experimental data are available, incorrect data analysis will lead to incorrect conclusions regarding the performance of the system. It is important to recognize that both reduction and analysis are purely mathematical in nature.

3.1 Reduction

Data reduction is the process by which raw data are converted to the quantity of interest. Examples of data reduction include:

- a voltage output from a thermocouple is converted to temperature;

- a gas chromatograph signal is converted to mole ratios; and

- a volume of titrant is converted to an analyte concentration.

Data reduction is generally accomplished using correlations (e.g. a calibration curve) or a knowledge of the underlying mechanism by which the measured quantity is related to the quantity of interest (e.g. force F may be computed from accelerometer measurements a if the mass m of the body is known using Newton's second law, $F = ma$). Chapter 5 details the relationships by which data reduction may be achieved for this course.

3.2 Analysis

Data analysis covers a broad range of topics, including statistics, developing correlations using curve fitting, or fitting a model to data. For the purposes of this course, each of these may be carried out using any spreadsheet software.

3.2.1 Statistical Analysis

Statistical analysis is a very broad area, so this section will cover only the basics. For the purposes of this course, we will assume that all results are drawn from a normal (Gaussian)

probability distribution function $p(x)$, which is described by

$$p(x) = \frac{1}{\sigma\sqrt{2\pi}}e^{-\frac{(x-\mu)^2}{2\sigma^2}}. \tag{3.1}$$

Here, μ is the mean given by

$$\mu = \int_a^b xp(x)dx \approx \frac{1}{N}\sum_{i=1}^N x_i, \tag{3.2}$$

and σ is the standard deviation given by

$$\sigma = \sqrt{\int (x-\mu)^2 p(x)dx} \approx \sqrt{\frac{\sum_{i=1}^N (x_i-\mu)^2}{N-1}}. \tag{3.3}$$

The approximate equalities ($\approx$) are due to the Central Limit Theorem, which states that a sufficiently large but finite number of observations of a distribution will exhibit mean μ and standard deviation σ related to those of the true distribution as stated in these equations.

The general probability distribution function $p(x)$ describes the probability p of making a measurement equal to x at a fixed value of the independent variable. The parameters μ and σ indicate the most probable measurement and the degree of spread which the measurements exhibit, respectively.

T-Test

A t-test allows one to objectively answer the question, "Are the results from two sets of experiments different in a statistical sense?" The t statistic is essentially a score related to the likelihood that the means μ_A and μ_B are significantly different given the number of observations from each distribution n_A and n_B with standard deviations σ_A and σ_B, and is given by

$$t_{AB} = \frac{\mu_A - \mu_B}{\sqrt{\frac{\sigma_A^2}{n_A} + \frac{\sigma_B^2}{n_B}}}. \tag{3.4}$$

Computing the probability that the two means are significantly different from the t statistic t_{AB} may only be done numerically by inverting the t probability density function, so tables are used common cases (e.g. Table 3.1). Three types of t-tests are available and the tabular values will differ for each. The three types are:

1. matched pair test in which the two samples have an equal number of values ($n_A = n_B$) and standard deviations ($\sigma_A = \sigma_B$);

2. homoscedastic, which assumes that the standard deviations of the two samples are equal ($\sigma_A = \sigma_B$); and

3. heteroscedastic, which allows different standard deviations for both samples may differ.

Table 3.1: Minimum t-statistic value for significance level $\alpha = 0.05$

DOF	$\mathbf{t_{min}}$
1	12.71
2	4.30
3	3.18
4	2.78
5	2.57
6	2.45
7	2.37
8	2.31
9	2.26
10	2.23
11	2.20
12	2.18
13	2.16
14	2.14
15	2.13

Alternatively, this calculation may be carried out in Microsoft Excel using the *tinv()* function and in MATLAB using the *ttest2()* function. For any t-test table or function, one needs to compute the degrees of freedom (DOF), which is simply $n_A + n_B - 2$. In any statistical test, it is impossible to say with absolute certainty that the two samples are different. Therefore, the t-test is used to ascertain the probability that the two samples are drawn from the same distribution (i.e. $\mu_A = \mu_B$). This is called the "Null Hypothesis," denoted as H_0, as the test determines the likelihood that the difference $\mu_A - \mu_B$ is zero (null). The probability returned by inverting the t-statistic is the likelihood that H_0 is true. Accepting that H_0 is true or false is based on an arbitrary guideline: if $p < \alpha$, then H_0 is false. Generally, $\alpha = 0.05$, meaning that the data indicate greater than 95% probability that H_0 is false, or less than 5% chance that H_0 is true.

Analysis of Variance

Analysis of variance (ANOVA) is essentially a t-test for answering the null hypothesis H_0 that the means of more than two samples are all statistically equal.

The calculations required for ANOVA are very straightforward. Three types of residual metrics are calculated, corresponding to the total, treatment, and error sum of squares (SST, SSA, and SSE, respectively). These parameters are defined as

$$SST \equiv \sum_{i=1}^{k} \sum_{j=1}^{n} (y_{ij} - \bar{\bar{y}})^2, \tag{3.5}$$

$$SSA \equiv SST - SSE, \tag{3.6}$$

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Table 3.2: Minimum F-ratio value for significance level $\alpha = 0.05$

DOF_1	DOF_2						
	1	2	3	4	5	6	7
1	161.4476	18.5128	10.1280	7.7086	6.6079	5.9874	5.5914
2	199.5000	19.0000	9.5521	6.9443	5.7861	5.1433	4.7374
3	215.7073	19.1643	9.2766	6.5914	5.4095	4.7571	4.3468
4	224.5832	19.2468	9.1172	6.3882	5.1922	4.5337	4.1203
5	230.1619	19.2964	9.0135	6.2561	5.0503	4.3874	3.9715
6	233.9860	19.3295	8.9406	6.1631	4.9503	4.2839	3.8660
7	236.7684	19.3532	8.8867	6.0942	4.8759	4.2067	3.7870
8	238.8827	19.3710	8.8452	6.0410	4.8183	4.1468	3.7257
9	240.5433	19.3848	8.8123	5.9988	4.7725	4.0990	3.6767
10	241.8817	19.3959	8.7855	5.9644	4.7351	4.0600	3.6365

and

$$SSE \equiv \sum_{i=1}^{k} \sum_{j=1}^{n} (y_{ij} - \bar{y}_i)^2, \tag{3.7}$$

for k treatments, n replications for each treatment, y_{ij} the jth response for treatment i, $\bar{y}_i$ the mean response for the ith treatment, and $\bar{\bar{y}}$ is the grand mean of all data.

Once the sums of squares have been calculated, the corresponding mean squares MST, MSA, and MSE are computed. These are given by

$$MST \equiv \frac{SST}{kn - 1}, \tag{3.8}$$

$$MSA \equiv \frac{SSA}{k - 1}, \tag{3.9}$$

and

$$MSE \equiv \frac{SSE}{k(n - 1)}, \tag{3.10}$$

where the denominator is the number of degrees of freedom related to each sum of squares.

Finally, the metric used to determine significance with ANOVA is the F-ratio, given by

$$F = \frac{MSA}{MSE}. \tag{3.11}$$

Determination of the probability that H_0 holds is achieved in the same way as for the t-test: the F distribution is inverted to determine the p-value corresponding to the F-ratio. This must be done numerically and is generally achieved using tabulated results available for common cases (Table 3.2). The inversion of the F distribution involves two distinct quantities: the degrees of freedom within each treatment ($DOF_1 = k(n-1)$) and the degrees of freedom between treatments ($DOF_2 = k - 1$).

Note that the ANOVA test described here is called a "balanced ANOVA" due to the use of an equal number of samples for each treatment. ANOVA may be generalized to address

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unbalanced sampling (unbalanced ANOVA). When multiple dependent variables are measured, a multivariate analysis of variance (MANOVA) may be employed. These functions are implemented in MATLAB in the *anova1()*, *anova2()*, and *anovan()* functions, where the former two both require balance and respectively require one and two dependent responses; the latter is a more general function which allows analysis of balanced or unbalanced data with unlimited dependent responses. The Data Analysis Add-In also imparts ANOVA functionality on Microsoft Excel, though in a more limited scope.

3.2.2 Curve Fitting

Correlation and mechanistic models differ substantially in the information they provide regarding the system to which they are applied. However, the methods required for their application are essentially identical. A general algorithm for fitting any curve to any set of data is as follows:

1. Determine the mathematical function which will be fitted to the data. This may be a line, an equation of state, a mathematical description of a physical law, or any other function.

2. Determine a metric which will be used to determine the "goodness-of-fit." This is generally the sum of the squared residuals $\sum (y - \hat{y})^2$, where y and $\hat{y}$ are respectively the model and data values at a given x. This is called the least squares method. The metric is called a cost function.

3. Apply a suitable minimization technique which varies the fitting parameters such that the specified metric is minimized. In the case of fitting a line, linear algebra may be used to uniquely determine the best-fit coefficients. More generally, a variety of algorithms have been developed to affect such minimization.

Determining the fitting function

Selection of the fitting function depends largely on the goal of the analysis. If one simply needs a correlation between the independent and dependent variables, a line or polynomial will usually be selected. The coefficients derived from such a fit offer little or no insight into the behavior of the system and simply map one variable to the other. If, on the other hand, more insight into the mechanisms underlying the system's behavior, a model function which is a mathematical description of the system is needed. In this case, the fitting parameters should give some quantitative information about the system which is not available from a simple correlation. Thus, the trade-off between fitting a correlation and a model is usually between simplicity and information.

Determining the cost function

A cost function C is generally a metric which describes how well the fitting function relates to the data. This quantity is usually a scalar quantity. Methods for optimizing non-scalar cost functions are very complex and beyond the scope of this text. Many problems which

appear to have multiple cost functions c_i may be solved using standard methods by simply summing the cost functions (i.e. $C \equiv \sum c_i$), so this limitation is not as severe as it may initially seem.

The cost function selection may be suggested by the physical model or by experience. The most commonly employed cost functions are called norms, which are simply some measure of distance from some reference state, such as the location of data points. Norms are always positive, real, and scalar and are denoted by $\|y - \hat{y}\|_X$, where y is some fitting function, $\hat{y}$ are the data, and X is some notation denoting the type of norm (e.g. $\| \|_{L_2}$ is called the energy norm, whereas $\| \|_{L_2}$ or simply $\| \|_2$ is the least squares norm).

The norm which is most often used is the least-squares norm $\| \|_2$, which is defined as

$$\|y - \hat{y}\|_2 \equiv \sqrt{\int (y - \hat{y})^2 dx} \approx \sqrt{\sum (y - \hat{y})^2}. \tag{3.12}$$

This norm is related to the Euclidean distance between the fitting function and the data, effectively quantifying how close the fitting function comes to passing through each data point. Thus, unless some physical reason suggests another norm, $\| \|_2$ is likely appropriate. For mathematical and computational efficiency reasons, the square of this norm is generally selected as the cost function C,

$$C = \sum (y - \hat{y})^2. \tag{3.13}$$

Global minimization of C therefore ensures that the fitting function y passes as close as it possibly can to the data $\hat{y}$.

The least-squares method is based on the assumption that the residuals $r_i = y(x_i) - \hat{y}_i$ are normally distributed. This assumption is most easily examined by plotting r_i against x: if no trend is apparent (i.e. r_i are scattered randomly around 0; Fig. 3.1A), then the assumption should hold. Otherwise, as in the case of "fanning," (Fig. 3.1B) a transformation needs to be applied to the data and fitting function values (i.e. y and $\hat{y}$ become $\bar{y}$ and $\bar{\hat{y}}$, where the $^-$ denotes the transformed value). The most commonly applied transformations are:

- Logarithmic transform: $\bar{y} = \log y$;

- Square root transform: $\bar{y} = \sqrt{y}$;

- Inverse square root transform: $\bar{y} = \frac{1}{\sqrt{y}}$;

- Exponential transform: $\bar{y} = e^y$; and

- Power transform: $\bar{y} = y^x$, where x is some constant.

Once the transformed values are fitted, the residual plot should again be constructed to examine whether the residuals are randomly distributed about the $r = 0$ line.

Minimizing the fitting metric

Mathematicians since Isaac Newton have attempted to find ways to minimize the value of cost functions. The mathematics underlying these algorithms are often complex, but the
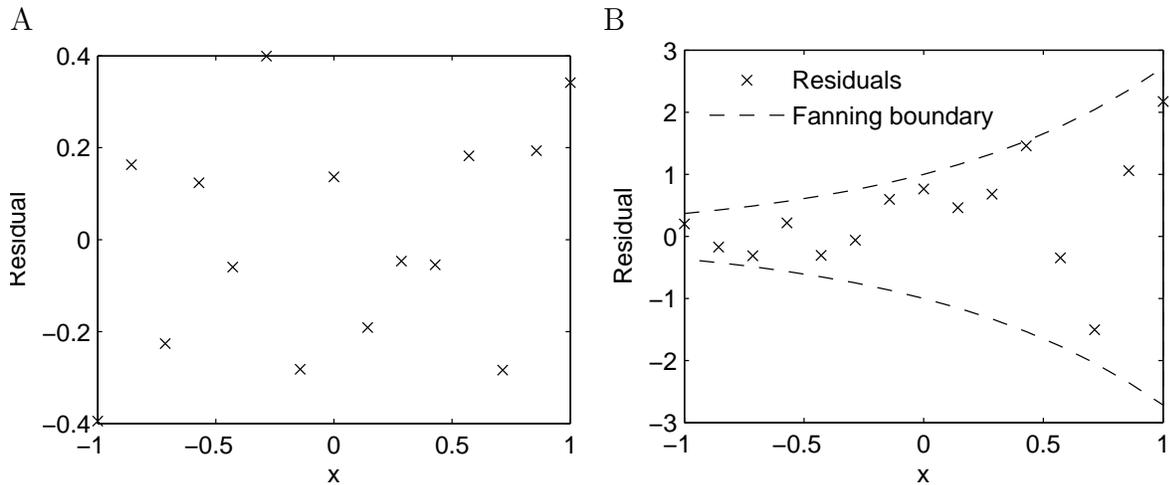
Figure 3.1: Normally distributed residuals will be randomly dispersed about the line $r = 0$ (A), whereas non-normally distributed residuals will exhibit obvious trends, such as "fanning" (B).

basic idea is simply to keep changing the value of the fitting parameters such that the value of the cost function decreases. Under certain conditions, this can lead to finding minima which do not globally minimize C. However, by formulating C as was done in Eqn. (3.13), this problem is often eliminated.

Many algorithms for cost function minimization are available, including quasi-Newton, Nelder-Mead simplex, conjugate gradient, steepest descent, genetic algorithm, simulated annealing, branch and bound, greedy algorithms, and other methods. Microsoft Excel's solver allows one to select between the quasi-Newton and conjugate gradient methods using its *Solver* tool. MATLAB is equipped with the Nelder-Mead simplex solver (*fminsearch*) by default, with many other options available through purchase of the Optimization and/or Curve Fitting Toolboxes.

Parameter constraints Fitting parameters for mechanistic models often requires the application of constraints to the parameter values. For example, it does not make sense for a characteristic time to be negative, so such a parameter must be constrained to values greater than zero. While there are many methods for enforcing constraints, the simplest and often most effective is known as the Courant-Beltrami penalty function. This method augments the cost function C with a term indicating the extent to which any constraints g are being violated. The augmented penalty function $\hat{C}$ is defined as

$$\hat{C} \equiv C + k \sum_{i=1}^{n} g_i^2, \tag{3.14}$$

where k is a large constant (e.g. 10^8), n is the number of constraints, and g_i is the extent to which the constraint is violated. For example, if the fitting parameters a_i must be non-

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negative,

$$g_i = 0 \qquad\qquad \text{if } a_i \geq 0 \qquad\qquad (3.15)$$
$$= |a_i| \qquad\qquad \text{if } a_i < 0.$$

3.3   Summary

Data reduction and statistical analysis allow the well-trained engineer to extract the maximum amount of information from a small amount of available data. Data reduction allows one to back out the underlying physical parameters which allow the results of an experiment to be generalized to a broad range of operating conditions by relating the known physicochemical features of the process to the observed behavior.

The proper use of statistical analysis allows one to objectively answer the question, "Does it matter if I operate this process under condition x or condition y?" Combining this with curve fitting methods allows the fitting of a response surface to the data, answering the questions, "Is this difference big enough to worry about?" and, if the answer is affirmative, "How can I then maximize the performance of this process by manipulating the significant parameters?" Combining these techniques allows the knowledgeable engineer to maximize the performance of the available unit operations, thereby improving the overall efficiency and economic outlook of the process.

3.4   Additional Reading

- http://www.socialresearchmethods.net/kb/stat_t.php

- http://mathworld.wolfram.com/ANOVA.html

- http://www.statsoft.com/textbook/anova-manova/

Chapter 4

Reporting Results

When giving a report in any format, success is contingent on knowing the audience to which the report will be given. The report should be tailored to the audience by defining terms which the audience may not know, giving (or excluding) background information based on the audience's background, and even possibly bringing food to an oral presentation according to custom. Care should always be taken to ensure that the the report appears polished and professional.

4.1 Written Reports

In a written report, the methods and results sections must contain only facts. Any subjective interpretation should be left to the introduction and discussion. The first page should include the title, list of authors, and the abstract. The introduction should start on the following page, followed by the other sections. All tables and figures should be appended at the end of the report rather than embedded in the text.

All written reports must be submitted as a single PDF file. Written reports may be typeset using any word processing program. Templates will be provided for Microsoft Word 2007 (.docx) and *LaTeX* (.tex). *LaTeX* is a freely available typesetting program which uses tags similar to html to produce appropriately formatted text (see Appendix A for a basic overview).

4.1.1 Abstract

The abstract is a one-paragraph executive summary of the report and should capture all of the essential features of the report. The abstract is the most-read portion of any report or article, so it should be written carefully. It is essentially comprised of a 1-2 sentence summary of each of the following sections of the paper. Critical numerical results should be given explicitly.

4.1.2 Introduction

The introduction should set the stage for the rest of the report by supplying important background information, stating why the experiment is important, and place your experi-

ments in the context of the literature. Generally, no subheadings should occur within the introduction.

4.1.3 Methods

The description of methods should be of sufficient detail that a knowledgeable reader could reproduce your experiments. Specifically, the following should be stated explicitly:

- the make, model, and manufacturer of any equipment used;

- the concentration, purity, and manufacture of any reagents used; and

- a detailed description of the statistical methods used.

Each of these may appear under an appropriate subheading (e.g. *Apparatus*, *Materials*, and *Statistical Methods* would be appropriate subheadings for the items listed above). Any non-obvious terms should be explicitly defined, using equations as necessary. A very brief example of a description of methods is given here.

> A baffled, flat-bottom acrylic tank (model 4F63; Chemineer, Dayton, OH) was placed on an electronic load cell (HW-G; A&D Mercury Pty,Ltd; Thebarton, Australia). The load cell had a resolution of 0.1 N. The tank was filled with corn syrup (Karo, Louisville, KY). The syrup was agitated at a variety of frequencies using a motor with variable gear ratio (model BP11; Chemineer) using H-3, P-4, and marine impellers (Chemineer). Standard agitation tank dimensions were used (see McCabe et al., 2001, p. 463).
>
> Thrust and frequency were nondimensionalized as the axial thrust number N_t and the Reynolds number N_{Re}. N_t was defined as
>
> $$N_t = \frac{F_t}{\rho n^2 D_a^4},\tag{4.1}$$
>
> where F_t is the axial thrust force, ρ is the density of the fluid, n is the angular impeller velocity, and D_a is the impeller diameter. N_{Re} was defined as
>
> $$N_{Re} = \frac{D_a^2 n \rho}{\mu},\tag{4.2}$$
>
> where μ is the Newtonian fluid viscosity. Linear regression was used to examine whether N_t was dependent on N_{Re}.

4.1.4 Results

The results section should explicitly state numerical results (usually in the form of a mean ± standard deviation). All figures showing results should also be explicitly referenced in the text. Tables of data may also be included if the data do not lend themselves to presentation in graphical format. If so, these tables should be explicitly referenced in the text. Data presented in figure format should not also be included in tabular format.

4.1.5 Discussion

The discussion should attempt to put the results in the context of the literature, particularly through critical comparison of data. This section also allows the author(s) to offer interpretation of the results, including why their results disagree with the literature, why their results are of interest, and suggest future work based on the present findings. A short conclusion paragraph is often used at the end of the discussion section to summarize the key points of the work. Alternatively, a separate heading may be used for the conclusions if a longer summary is warranted. In this latter case, key points are often listed in a bulleted list.

4.1.6 References

Every report should include at least five references in a bulleted list, which may include textbooks and research articles. This text may also be referenced as appropriate. Article references should include the author(s), title, journal, year, volume, and inclusive page numbers. Book references should include the author(s), editor(s) (if any), chapter title, book title, year, and relevant page numbers. The particular order of these items in the references is left to the authors, but consistency should be observed within the list. References should be cited at the appropriate location in the text using an (author, year) format, such as (Reilly et al., 2010).

4.1.7 Figures

The figures and captions are often the only part of an article that a reader will consider after selecting the article based on the abstract. Thus, particular care should be taken to make the figures self-explanatory using appropriate captions. Each figure caption should describe what the figure shows and what the reader should take away from the figure. All axes and data series should be clearly labeled. All text should be easily visible at the final print size of the figure. Figures should generally include data as individual points without connecting lines. The points should be located based on the mean value of any repetitions, with error bars indicating standard deviations. Trend lines, fitted model functions, and/or trends from the literature should also be included if possible. The key idea of a figure is to convey as much information as possible using as little space as possible.

4.2 Oral Reports

In an oral report, the structure is much less rigid. It is, of course, generally best to maintain the format of a written report in that an introduction precedes the description of methods. However, it may be that each part of the experiment is described in a subsection of the presentation (i.e. multiple sequences of methods, results, and discussion). The presentation of methods and results is generally less rigorous, while the focus is placed more on discussing the take-home message of each element.

Visual aids form a critical part of any oral report. These aids may include slides, videos, animations, photographs, drawings on a chalkboard, a piece of equipment, a synthesized product, or anything else that helps the audience understand the material presented.

Chapter 5

Experimental Systems

This chapter gives a cursory overview of the five experimental systems which will be used for this course, as well as references to more exhaustive treatments of each system. These systems are:

1. continuous flow reactors,

2. a batch distillation column,

3. a pumping for quantifying pumping performance,

4. a packed bed reactor for gas-liquid absorption with reaction, and

5. a gas membrane separator.

These systems are commonly employed in industry and allow you to apply the fundamentals you have learned in other courses to practical processes.

5.1   Continuous Flow Reactors

Chemical reactors are everywhere, from combustion engines to cooking ovens. The ability to design a chemical reactor well is one of the essential skills which sets a chemical engineer apart from other types of engineers. Many idealized reactor models are available in the literature, with the most common presented here as an overview.

Continuous Stirred Tank Reactor   A continuous stirred-tank reactor (CSTR) is an idealized reactor model in which it is assumed that no spatial inhomogeneities exist in temperature or concentration. The feed stream is input into a well-mixed tank. The effluent is the same composition as the contents of the tank. Thus, inputting reagents to the CSTR effectively dilutes them, decreasing the concentration of the reactants. The CSTR is therefore desirable for reactions with kinetics below order unity (i.e. when the reaction rate is inversely related to reactant concentration).

Plug Flow Reactor A plug flow reactor (PFR) is an idealized reactor model in which it is assumed that the concentration and temperature vary only along the axis of flow (i.e. no radial variations exist due to turbulent mixing effects, and the fluid velocity is high relative to any axial dispersion effects due to diffusion). Thus, the reactant concentrations decrease with distance from the feed. The temperature may increase or decrease along the axis, depending on whether the reaction is exothermic or endothermic. The PFR is therefore desirable for reactions with kinetics greater than order unity (i.e. when the reaction rate is an increasing function of reactant concentration).

Laminar Flow Reactor A laminar flow reactor (LFR) is an adaptation of the PFR model from turbulent to laminar flow. In this model, the radial position of the fluid determines its residence time within the reactor: since the fluid velocity is maximum at the center of the pipe, it has less time to react than the fluid near the walls. Thus, axial and radial concentration gradients exist. The LFR is therefore useful for highly viscous fluids, such as polymers, which are difficult to mix using mechanical agitators and may not flow in the turbulent regime due to large viscous and complex fluid effects.

5.1.1 Recommended Experiments

Some ideas for experiments using the chemical reactor apparatus in the unit operations laboratory are:

- Quantifying the reaction rate equation for a given reaction;

- Determining which of the continuous flow reactor models is most appropriate for a given reaction/reactor combination;

- Estimating the errors in reactor performance due to the use of the application of one or more of the continuous flow reactor models;

- Estimating the mixing time of the CSTR;

- Quantifying the temperature effects on the reaction rate constant; and

- Quantifying the effect of volumetric flowrate on reactant conversion in each reactor type.

5.1.2 Reference Material

- Walas, S.M., Section 23: Chemical Reactors. In: Perry, R., Green, D., Maloney, J., *Perry's Chemical Engineering Handbook*, 6th ed., McGraw Hill, 1984.

- McCabe, W., Smith, J., Harriott, P., *Unit Operations of Chemical Engineering*, 7th ed., McGraw Hill, 2004.

- Levenspiel, O., *Chemical Reaction Engineering*, 3rd ed., John Wiley & Sons, 1999.

- Smith, J.M., Van Ness, H.C., Abbott, M.M., *Chemical Engineering Thermodynamics*, 6th ed., McGraw Hill, 2001.

5.2 Batch Distillation

Thermal distillation is a process by which two or more chemical species are separated on the basis of their differing vapor pressures: by heating the feed stock, the more volatile components will tend to leave the column in the vapor effluent (distillate), while the less volatile will leave the column in the liquid effluent (bottoms). This process is ubiquitous in industry and is used to separate and purify everything from crude oil to alcoholic spirits.

5.2.1 Recommended Experiments

Some ideas for experiments using the batch distillation column apparatus in the unit operations laboratory are:

- Determining the minimum reboiler heating rate to achieve a 95% pure distillate;

- Generating a temperature-composition diagram for the column;

- Calculating the thermal efficiency of the column over time;

- Determining the overall column mass efficiency; and

- Minimizing the time required to obtain a reboiler liquid purity of 95%.

5.2.2 Reference Material

- Seader, J.D., Siirola, J.J., Barnicki, S.D., Section 13: Distillation. In: Perry, R., Green, D., Maloney, J., *Perry's Chemical Engineering Handbook*, 6th ed., McGraw Hill, 1984.

- McCabe, W., Smith, J., Harriott, P., Ch. 21: Distillation. In: *Unit Operations of Chemical Engineering*, 7th ed., McGraw Hill, 2004.

- Wankat, P.C., *Equilibrium Staged Separations*, Prentice Hall, 1988.

- Smith, J.M., Van Ness, H.C., Abbott, M.M., *Chemical Engineering Thermodynamics*, 6th ed., McGraw Hill, 2001.

5.3 Pumping Performance

Pumps are the most common unit in the chemical industry. Choosing a pump which is highly efficient at driving the flow in the process at hand will save time and money over the lifetime of the process. This experiment allows you to measure the input electrical energy, output work, and compute the overall efficiency of the pump under a variety of conditions.

5.3.1 Recommended Experiments

Some ideas for experiments using the pumping apparatus in the unit operations laboratory are:

- Quantifying the efficiency of the pump at various volumetric flowrates;

- Determining the role of viscosity on pumping efficiency;

- Quantifying the dependence of the pumping efficiency on the pipe loop length and/or head loss;

- Estimating the head loss resulting from various parts of the piping system; and

- Determining the cost of operating the pump at various volumetric flowrates.

5.3.2 Reference Material

- Boyce, M.P., Section 10: Transport and Storage of Fluids. In: Perry, R., Green, D., Maloney, J., *Perry's Chemical Engineering Handbook*, 6th ed., McGraw Hill, 1984.

- McCabe, W., Smith, J., Harriott, P., *Unit Operations of Chemical Engineering*, 7th ed., McGraw Hill, 2004.

5.4 Gas-Liquid Absorption

Gas-liquid absorption (GLA) is yet another commonly used separation process. GLA is used to transfer a species from the gas phase to the liquid phase. Thus, the liquid should be a good solvent for the desired solute but not for other species present in the gas feed. Mass transfer rates may be greatly increased by utilizing a solvent which chemically reacts with the solute.

5.4.1 Recommended Experiments

Some ideas for experiments using the GLA packed bed reactor in the unit operations laboratory are:

- Quantifying the mass transfer coefficient of carbon dioxide at various operating conditions;

- Calculating the reactor size required to remove 99% of carbon dioxide from the feed for various gas/liquid feed ratios; and

- Determining the thermal efficiency of the packed bed.

5.4.2   Reference Material

- Fair, J.R., Steinmeyer, D.E., Penney, W.R., Crocker, B.B., Section 14: Gas Absorption and Gas-Liquid System Design. In: Perry, R., Green, D., Maloney, J., *Perry's Chemical Engineering Handbook*, 6th ed., McGraw Hill, 1984.

- McCabe, W., Smith, J., Harriott, P., Ch. 18: Gas Absorption. In: *Unit Operations of Chemical Engineering*, 7th ed., McGraw Hill, 2004.

- Wankat, P.C., *Equilibrium Staged Separations*, Prentice Hall, 1988.

- Smith, J.M., Van Ness, H.C., Abbott, M.M., *Chemical Engineering Thermodynamics*, 6th ed., McGraw Hill, 2001.

- Levenspiel, O., *Chemical Reaction Engineering*, 3rd ed., John Wiley & Sons, 1999.

5.5   Gas Membrane Separation

Gas membrane separation is an increasingly important technology in which the affinity of a membrane for a solute gas molecule drives a separation of the solute from the feed gas. The feed gas is supplied on the shell side (i.e. outside the membrane). Two effluent streams leave the system: one on the shell side and one inside the membrane, called the permeate. In some processes, the shell effluent is actually the desired product, as in naval fire extinguishing systems when air is input and the membrane is used to remove oxygen from the air to create an anoxic stream used to extinguish the fire. In other processes, the permeate is the desired product.

In the gas membrane separation experiment, you will examine the effects of contacting patterns and feed flowrates on the performance of the separation unit. Specifically, the students may examine the behavior of the unit under cocurrent, countercurrent, and series-parallel flow patterns.

5.5.1   Recommended Experiments

Some ideas for experiments using the gas membrane apparatus in the unit operations laboratory are:

- Determining the mass transfer coefficient of oxygen through the membrane at different feed pressures and flowrates;

- Quantifying the effects of contacting patterns (cocurrent and countercurrent);

- Maximizing product gas flowrate relative to feed flowrate; and

- Determining the membrane length required to remove 99% of the oxygen from the feed.

5.5.2 Reference Material

- Henry, J.D., Prudich, M.E., Eykamp, W.E., Hatton, T.A., Johnston, K.P., Lemert, R.M., Lemlich, R., Moyers, C.G., Newman, J., Pohl, H.A., Pollock, K., Thien, MP., Section 22: Alternative Separation Processes. In: Perry, R., Green, D., Maloney, J., *Perry's Chemical Engineering Handbook*, 6th ed., McGraw Hill, 1984.

- McCabe, W., Smith, J., Harriott, P., Ch. 26: Membrane Separation Processes. In: *Unit Operations of Chemical Engineering*, 7th ed., McGraw Hill, 2004.

- Smith, J.M., Van Ness, H.C., Abbott, M.M., *Chemical Engineering Thermodynamics*, 6th ed., McGraw Hill, 2001.

Appendix A

LaTeX Reference

LaTeXis a markup language which automatically typesets your input into a usable output. Of greatest use in this course will be *pdftex*, which converts the tex input directly to a PDF file. LaTeXallows direct incorporation of captioned tables and figures without the headaches associated with performing these operations in Microsoft Word. This feature in particular makes LaTeXuseful for anyone who prepares lengthy documents containing tables and figures, as Word often gets bogged down trying to manage the arrangement of all of these objects. It is very frustrating trying to organize such a document in Word since moving one figure will result in a cascade effect moving all subsequent figures. Thus, while it may take some initial effort up front to learn LaTeX, it is usually time well spent. LaTeXis also open source, which means it is completely free and is very well documented online.

The basic components of any LaTeXinput file are a class declaration, a preamble (a section which calls all of the packages you might need to format your document as you see fit), and the actual document code enclosed in the *document* environment. Thus, the only code you need to get started is:

```
\documentclass{article}
\begin{document}
  your text here
\end{document}
```

The course website gives a much more detailed template which simply requires you to type in the text for the various sections just like you would if you were using Word, then compile the resulting file using the

A.1 Command Reference

LaTeXis very easy to use once you have a grasp of the basics. Comments are preceded by %. Like HTML, it is comprised of various environments denoted in the source code by tags. The basic environment, `\par`, is a paragraph. Since this is so common, simply including a blank line will generate a new `\par` environment by default. Inline environments and many commands may be used within the `\par` environment. The most common inline environments are `$ $` for math, `\emph{}` which is used for emphasis/italics, and `\textbf{}` for bold type. `\section{}`, `\subsection{}`, and `\subsubsection{}` allow you to include

automatically numbered headers.

Additional environments allow special emphasis on things like equations or sections of code. For example, to include a display equation, the input has the form

```
\begin{equation}
  z_i^2=x_i^2+y_i^2
  \label{Eqn.PythagoreanTheorem}
\end{equation}
```

which has the output

$$z_i^2 = x_i^2 + y_i^2 \tag{A.1}$$

and may be referenced as `Equation \ref{Eqn.PythagoreanTheorem}`, which gives the output Equation A.1. For listing code, one may use the *verbatim* environment, but this omits indentation and can make deciphering the code difficult. It is therefore usually preferable to use the *lstlisting* environment, which requires the inclusion of `\usepackage{listings}` in the document preamble. Then, using the command `\begin{lstlisting}...\end{lstlisting}` will display the code as desired.

A.2   Floating Environments

Floating environments, or "floats," are automatically positioned by LaTeXto position them appropriately on the page. The most common floats are figures and tables. Sample code to generate a figure and a table are given here. These examples are pulled directly from the LaTeXtemplate for this course. Floats are automatically labeled and numbered according to the order of their appearance in the document, so it is unnecessary to keep track of table/figure numbers manually or to include "Figure 1" or "Table 1" at the beginning of the captions.

Including a figure

This input will include the graphics file *distillationcolumn.jpg* from the relative path *images/* in the output file. The figure will appear at 50% of the width of the text `\textwidth` with the caption, "This is a sample figure." The figure may be referenced within the text as `Fig. \ref{Fig.DistillationColumn}`, which gives the output Fig. A.1.

```
\begin{figure}
  \centering
  \includegraphics[width=0.5\textwidth]{images/distillationcolumn.jpg}
  \caption{Here is a picture of a distillation column.}
  \label{Fig.DistillationColumn}
\end{figure}
```

The full output is shown in Fig. A.1.

Including a table

This input will create a table in the output file. The table will have three columns due to three characters in the argument after the `\begin{tabular}` command with an alignment

Figure A.1: Here is a picture of a distillation column.

specified by the alignment characters in that argument (where c, r, and l are centered, right, and left alighment, respectively, and the | inserts a vertical line between the columns). The `\hline` command inserts a horizontal line between consecutive rows. Each row must be concluded with a newline command `\\`, and each column within each row is concluded by &. The table is referenced in the text as `Table \ref{Table.SampleResults}`, which appears as Table A.1.

```
\begin{table}
  \centering
  \caption{Sample Table of Results}
  \begin{tabular}{c|cc}
    Time & Temperature & Concentration \\
    $s$ & $^{\circ}C$ & $mol/L$\\
    \hline
    5 &35 & 0.108\\
    10 &40 & 0.272\\
    15 &42 & 0.351\\
    \hline
  \end{tabular}
  \label{Table.SampleResults}
```

\end{table}

This outputs the table:

Table A.1: Sample Table of Results

Time	Temperature	Concentration
s	$^\circ C$	mol/L
5	35	0.108
10	40	0.272
15	42	0.351

A.3   Additional References

There are plenty of detailed LATEXreferences online which can fill you in on the details of the various commands. The ones I use most frequently are given here.

- LATEXintegrated with Google Docs

- Wikibooks LATEX

- Check your equation typesetting online (saves time if you're compiling a large file and you want to check just one equation)

- LATEXword counter (just paste your entire file into the box and counts the words in the resulting document)

- Natbib referenec sheet (natbib is a very useful package which allows you to keep all of your bibliographic entries in a database)

- JabRef - create and manage a bibliographic database for use with natbib

Appendix B

MATLAB Reference

MATLAB is a higher-level language that allows the engineer to focus more on algorithm development than syntax. MATLAB has many built-in math functions which allow you to efficiently solve most math problems without writing lots of code. Contrary to popular belief, MATLAB is a compiled language, so well-written MATLAB code will often perform nearly as well as well-written C code, though there are always exceptions.

For the purposes of this class, MATLAB may be used instead of Microsoft Excel to design an experiment using statistical DOE (Chapter 2), reduce data, and analyze results using statistical methods. MATLAB (and the relevant toolboxes which are available to you through the university) has built-in functions which perform all of the statistical analyses you are likely to require for this course. You may download MATLAB and toolboxes licensed by the university here.

Table B.1: MATLAB Functions for Statistical Design of Experiments

Function	Utility
*fracfactgen()**	Generate a fractional factorial design
*fracfact()**	Generate a full-resolution two-factor factorial design
*bbdesign()**	Box-Behnken design for response surface characterization
*cdesign()**	Central composite design for response surface characterization
*candgen()**	D-optimal design for response surface characterization
*regstats()**	Analyze a regression model on the current data
*rstool()**	Interactive response surface modeling
regress()	Find linear effects and confidence intervals
ttest()	One-sample and paired-sample t-test
ttest2()	Two-sample t-test
anovan()	N-way analysis of variance (ANOVA)

*These functions require installation of the Statistics Toolbox.

B.1 Examples

To assist you in properly utilizing MATLAB to design and analyze your experiments, some examples are presented here.

B.1.1 Initial Screening Experiment

A screening experiment is used to determine which independent variables have a significant effect on the dependent variables (see Chapter 2). Efficient design of such an experiment will allow you to obtain the maximum information from a minimum number of experiments, which is particularly useful for a course with limited time in the lab. In this example, a fractional factorial design is constructed to examine the role of three independent variables (feed concentration C, temperature T, and pressure P) on a single dependent response variable (overall reaction rate R).

The initial design may be developed in MATLAB as follows:

```
X=fracfact('C T P');
```

The resulting matrix X indicates the values for each variable, where -1 is the lower bound and 1 is the upper bound. For example, if we have decided to perform experiments within the ranges

- $0.1\ M \le C \le 1.0\ M$,

- $25°C \le T \le 50°$, and

- $1.0\ bar \le P \le 2.0\ bar$

for our independent variables, then if the third row of X has the values $\begin{bmatrix} -1 & 1 & -1 \end{bmatrix}$ would mean that the values of the independent variables for the third experiment in the series should be: initial concentration 0.1 M, temperature 50°C, and pressure 1.0 bar.

Once the designed experiments have been carried out and the response R has been quantified under each set of conditions, the experiment may be analyzed using `anovan()` to determine which of the independent variables is significant. The function `\regress()` may also be used to estimate the magnitude of the effects. The first step is to map the independent variable values from the normalized space $\begin{bmatrix} -1 & 1 \end{bmatrix}$ to the actual variable space dictated by the limits:

```
xlims=[0.1 1.0; 25 50; 1.0 2.0];%limits of independent variables
for(i=1:size(xlims,1))%remap each column
X(:,i)=xlims(i,1)+(xlims(i,1)-xlims(i,2)/(1-(-1))*(X(:,i)+1);
end
```

This modified form of X may be input directly to the statistical analysis functions to give regression coefficients which are based on the actual, rather than the normalized, variable values.

```
Xin={X(:,1) X(:,2) X(:,3)};%format the design matrix
p=anovan(R,Xin,'varnames',{'C';'T';'P'});%perform n-way ANOVA
b=regress(R,X);%Estimate the effect magnitudes
[p,b]%output the results
```

Any independent variable for which $p < 0.05$ is deemed statistically significant. The magnitude b of each effect is computed whether or not the effect is significant. This is done by assuming that the dependent variable varies linearly with each independent variable (or combination thereof, called 'interactions').

If the measured reaction rates R were $[6.97 \quad 12.0 \quad 9.62 \quad 14.5 \quad 8.34 \quad 10.2 \quad 9.51 \quad 13.2]^T$, ANOVA would indicate p values of 0.504, 0.004, and 0.0234 for C, T, and P, respectively. Thus, both temperature and pressure had a statistically significant effect on the overall reaction rate, while the initial concentration did not. The vector $b = [-0.3242 \quad 0.1730 \quad 2.7740]^T$ indicates that R increases by 0.173 units for a one degree rise in temperature, while an increase in pressure of one bar increases R by 2.774 units. The first value in b is not significantly different from zero (as indicated by a p value greater than 0.05) and should therefore be omitted when predicting R. Note that these values for b are based on linear regression and are therefore approximate, as we would not expect the reaction rate to increase linearly with temperature. Therefore, once we have established which factors significantly impact our response variable, a more detailed followup study may be undertaken to examine the detailed, potentially nonlinear, relationship between these variables. This is covered in the following section.

B.1.2   Response Surface Experiment

There are numerous methods by which a response surface experiment may be designed. Traditional methods (e.g. central composite and Box-Behnken designs) require a very low number of experiments for a given experimental resolution, but are only effective at resolving linear effects and their interactions. In the former example, we estimated a linear effect on the rate of reaction for temperature. The measured linear effects are usually reliable over small changes in the independent variable, even if the general response is nonlinear. However, we know that the dependence of reaction rate on temperature is generally not linear (indeed, it is generally exponential in the absence of mass transport limitations). Thus, a linear estimate will give significant errors even when measured over a small temperature range.

More recently, the focus has shifted to the development of designs capable of accurately measuring parameters for intrinsically nonlinear responses. The most prevalent method for this purpose is the d-optimal class of designs. There are a variety of such designs implemented in MATLAB's Statistics Toolbox. The code example here gives four methods for generating the design matrix X:

```
nruns=8;%total number of experiments
X_BB=bbdesign(2);%create the design matrix (Box-Behnken)
X_CC=ccdesign(2);%create the design matrix (central composite)
X_DO=candgen(2,'purequadratic');%create the design matrix (d-optimal)
X_CE=cordexch(2,nruns,'purequadratic');%d-optimal coordinate exchange
```

Note that the last two (d-optimal) designs require input about the expected form of the response surface. This input allows the design matrix to account for anticipated nonlinearities in the response.

As mentioned above, linear estimates are often sufficient for very small ranges of an independent variable, and quadratic estimates are often even better for a larger range of the variable. Thus, even though the true response may result from an exponential dependence on temperature, it will be accurately captured by the quadratic model. Assume that the measured responses for the design generated using $X = candgen()$ are $R = [5.59 \quad 6.36 \quad 6.09 \quad 7.32 \quad 6.89 \quad 7.62 \quad 7.59 \quad 7.91 \quad 7.94]^T$, and that we fit them using purely quadratic response surface, using the code:

```
stats=regstats(R,X,'purequadratic');%perform the regression
p=stats.fstat.pval %get the p value
Rsq=stats.adjrsquare %adjusted R^2
b=stats.beta %response surface coefficients
```

This gives an adjusted R^2 value of 0.8531, meaning that about 85% of the variance in the data may be explained by the model terms. The coefficient array is $b = [0.543 \quad 0.0275 \quad 6.13 \quad - 0.0002 \quad -1.44]^T$. The fit is characterized by a p value of 0.0154, meaning it is significantly different than the mean surface (i.e. a plane of constant R equal to the mean of all measurements of R).

In this manner, we can quickly and easily design and analyze very efficient experiments: we now know which factors are significant and, to a high degree of accuracy, how these factors are related to the reaction rate. This is all achieved using only a few lines of code in MATLAB and a minimum number of experiments. Thus, the majority of your time and effort may be put into calibrating your apparatus and performing the required series of experiments. It is important to remember that, even if you use all the statistical methods in the world, the results will be meaningless if the data you input is inaccurate.