

# **Fundamentals of Food Process Engineering**

Third Edition

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# Fundamentals of Food Process Engineering

Third Edition

Romeo T. Toledo

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 Springer

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Library of Congress Control Number: 2005935292

ISBN-10: 0-387-29019-2            e-ISBN-10: 0-387-29241-1  
ISBN-13: 978-0-387-29019-5       e-ISBN-13: 978-0-387-29241-0

Printed on acid-free paper.

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9 8 7 6 5 4 3 2 1

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# Preface

Since the publication of the first edition in 1981 and the second edition in 2001, this textbook has been widely adopted for Food Engineering courses worldwide. The author expresses his gratitude to colleagues who have adopted this textbook and to those who have made constructive criticisms on the material. This new edition not only incorporates changes suggested by colleagues, but additional material has been added to include facilitated problem solving using a computer, and new food processing and food product technologies. New sections have been added in most of the chapters reflecting the current state of the technology. The expanded coverage may result in not enough time available in a school term to cover all areas; therefore, instructors are advised to carefully peruse the book and select the most appropriate sections to cover in a school term. The advantage of the expanded coverage is the elimination of the need for a supplementary textbook.

The success of this textbook has been attributed to the expansive coverage of subject areas specified in the Institute of Food Technologists model curriculum for food science majors in the United States of America and the use of examples utilizing conditions encountered in actual food processing operations. This theme continues in the third edition. In addition to the emphasis on problem solving, technological principles that form the basis for a process are presented so that the process can be better understood and selection of processing parameters to maximize product quality and safety can be made more effective. The third edition incorporates most of what was in the second edition with most of the material updated to include the use of computers in problem solving. Use of the spreadsheet and macros such as the determinant for solving simultaneous linear equations, the solver function, and programming in Visual BASIC are used throughout the book. The manual problem-solving approach has not been abandoned in favor of the computer approach. Thus, users can still apply the concepts to better understand a process rather than just mechanically entering inputs into a pre-programmed algorithm.

Entirely new sections include enthalpy change calculations in freezing based on the freezing point depression, evaporative cooling, interpretation of pump performance curves, determination of shape factors in heat exchange by radiation, unsteady-state heat transfer, kinetic data for thermal degradation of foods during thermal processing, pasteurization parameters for shelf-stable high-acid foods and long-life refrigerated low-acid foods, high-pressure processing of fluid and packaged foods, concentration of juices, environmentally friendly refrigerants, modified atmosphere packaging of produce, sorption equations for water activity of solid foods, the osmotic pressure and water activity relationships, vacuum dehydration, new membranes commercially available for food processing and waste treatment, and supercritical fluid extraction.

This edition contains much new hard-to-find data needed to conduct food process engineering calculations and will be very useful as a sourcebook of data and calculation techniques for practicing food engineers.

Athens, Georgia

Romeo T. Toledo

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# CHAPTER 1

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# Review of Mathematical Principles and Applications in Food Processing

## 1.1 GRAPHING AND FITTING EQUATIONS TO EXPERIMENTAL DATA

### 1.1.1 Variables and Functions

A variable is a quantity that can assume any value. In algebraic expressions, variables are represented by letters from the end of the alphabet. In physics and engineering, any letter of the alphabet and Greek letters are used as symbols for physical quantities. Any symbol may represent a variable if the value of the physical quantity it represents is not fixed in the statement of the problem. In an algebraic expression, the letters from the beginning of the alphabet often represent constants; that is, their values are fixed. Thus, in the expression  $ax = 2by$ ,  $x$  and  $y$  represent variables and  $a$  and  $b$  are constants.

A function represents the mathematical relationship between variables. Thus, the temperature in a solid that is being heated in an oven may be expressed as a function of time and position using the mathematical expression  $T = F(x, t)$ . In an algebraic expression,  $y = 2x + 4$ ,  $y = F(x)$ , and  $F(x) = 2x + 4$ .

Variables may be dependent or independent. Unless defined, the dependent variable in a mathematical expression is one that stands alone on one side of an equation. In the expression  $y = F(x)$ ,  $y$  is the dependent and  $x$  is the independent variable. When the expression is rearranged in the form  $x = F(y)$ ,  $x$  is the dependent and  $y$  is the independent variable. In physical or chemical systems, the interdependence of the variables is determined by the design of the experiment. The independent variables are those fixed in the design of the experiment, and the dependent variables are those that are measured. For example, when determining the loss of ascorbic acid in stored canned foods, ascorbic acid concentration is the dependent variable and time is the independent variable. On the other hand, if an experiment involves taking a sample of a food and measuring both moisture content and water activity, either of these two variables may be designated as the dependent or independent variable. In statistical design, the terms “response variable” and “treatment variable” are used for the dependent and independent variables, respectively.

### 1.1.2 Graphs

Each data point obtained in an experiment is a set of numbers representing the values of the independent and dependent variables. A data point for a response variable that depends on only one independent variable (univariate) will be a number pair, whereas with response variables that depend on several independent variables (multivariate), a data point will consist of a value for the response variable and one value each for the treatment variables. Experimental data are often presented as a table of numerical values of the variables or as a graph. The graph traces the path of the dependent variable as the values of the independent variables are changed. For univariate responses, the graph will be two-dimensional, and multivariate responses will be represented by multidimensional graphs.

When all variables in the function have the exponent of one, the function is called first order and will be represented by a straight line. When any of the variables has an exponent other than one, the graph will be a curve in rectangular coordinates.

The numerical values represented by a data point are called the “coordinate” of that point. When plotting experimental data, the independent variable is plotted on the horizontal axis or “abscissa” and the dependent variable is plotted on the vertical axis or “ordinate.” The rectangular or Cartesian coordinate system is the most common system for graphing data. Both abscissa and ordinate are in the arithmetic scale and the distance from the origin measured along or parallel to the abscissa or ordinate to the point under consideration is directly proportional to the value of the coordinate of that point. Scaling of the abscissa and ordinate is done such that the data points, when plotted, will be symmetrical and centered within the graph. The Cartesian coordinate system is divided into four quadrants with the origin in the center. The upper right quadrant represents points with positive coordinates, the left right quadrant represents negative values of the variable on the abscissa and positive values for the variable on the ordinate, the lower left quadrant represents negative values for both variables, and the lower right quadrant represents positive values for the variable on the abscissa and negative values for the variable on the ordinate.

### 1.1.3 Equations

An equation is a statement of equality. Equations are useful for presenting experimental data because they can be mathematically manipulated. Furthermore, if the function is continuous, interpolation between experimentally derived values for a variable may be possible. Experimental data may be fitted to an equation using any of the following techniques:

1. Linear and polynomial regression: Statistical methods are employed to determine the coefficients of a linear or polynomial expression involving the independent and dependent variables. Statistical procedures are based on minimizing the sum of squares for the difference between the experimental values and values predicted by the equation.
2. Linearization, data transformation, and linear regression: The equation to which the data is being fitted is linearized. The data is then transformed in accordance with the linearized equation, and a linear regression will determine the appropriate coefficients for the linearized equation.
3. Graphing: The raw or transformed data is plotted to form a straight line, and from the slopes and intercept the coefficients of the variables in the equation are determined.

### 1.1.4 Linear Equations

Plotting of linear equations can be facilitated by writing the equation in the following forms:

1. The slope-intercept form:  $y = ax + b$ , where  $a$  = the slope, and  $b$  = the  $y$ -intercept, or the point on the ordinate at  $x = 0$ . The slope is determined by taking two points on the line with coordinates  $(x_1, y_1)$  and  $(x_2, y_2)$ , and solving for  $a = (y_2 - y_1)/(x_2 - x_1)$ .
2. The point-slope form:  $(y - b) = a(x - c)$ , where  $a$  = slope, and  $b, c$  represent coordinates of a point  $(c, b)$  through which the line must pass. When linear regression is used on experimental data, the slope and the intercept of the line are calculated. The line must pass through the point that represents the mean of  $x$  and the mean of  $y$ . A line can then be drawn easily using either the point-slope or the slope-intercept forms of the equation for the line.

The equations for slope and intercept of a line obtained by regression analysis of  $N$  pairs of experimental data are

$$a = \frac{\sum xy - (\sum x \sum y)/N}{\sum x^2 - [(\sum x)^2/N]}; \quad b = \frac{\sum y \sum x^2 - \sum x \sum xy}{N(\sum x^2 - [(\sum x)^2/N])}$$

The process of regression involves minimizing the square of the difference between value of  $y$  calculated by the regression equation and  $y_i$ , the experimental value of  $y$ . In linear regression,  $\Sigma(ax + b - y)^2$  is called the explained variation, and  $\Sigma(y_i - y)^2$  is called the random error or unexplained variation.

The ratio of the explained and unexplained variation is called the correlation coefficient. If all the points fall exactly on the regression line, the variation of  $y$  from the mean will be due to the regression equation, therefore explained variation equals the unexplained variation, and the correlation coefficient is 1.00. If there is too much data scatter, the random or unexplained variation will be very large, and the correlation coefficient will be less than 1.00. Thus, regression analysis not only determines the equation of a line that fits the data points, but it can also be used to test if a predictable relationship exists between the independent and dependent variables. The formula for the linear correlation coefficient is

$$r = \frac{N \sum xy - \sum x \sum y}{[[N \sum x^2 - (\sum x)^2][N \sum y^2 - (\sum y)^2]]^{0.5}}$$

$r$  will have the same sign as the regression coefficient  $a$ . Values for  $r$  that is much different from 1.0 must be tested for significance of the regression. The student is referred to statistics textbooks for procedures to follow in testing significance of regression from the correlation coefficient.

**Example 1.1.** The protein efficiency ratio (PER) of a protein is defined as the weight gain of an animal fed a diet containing the test protein per unit weight of protein consumed. Data is collected by providing feed and water to the animal so the animal can feed at will, determining the amount of feed consumed, and weighing each animal at designated time intervals. The PER may be calculated from the slope of the regression line for weight of the animal ( $y$ ) against cumulative weight of protein consumed ( $x$ ). The data expressed as  $(x, y)$  where  $x$  is the amount of feed consumed and  $y$  is the weight are as follows: (0, 11.5), (0, 12.2), (0, 14.0), (0, 13.3), (0, 12.5), (2.0, 16.8), (2.2, 16.7), (1.8, 15.2), (2.5, 18.4), (1.8, 16.8), (3.4, 22.8), (4.2, 22.5), (3.7, 20.7), (4.6, 25.3), (4.0, 23.5), (6.5, 28.0), (6.3, 29.5), (6.8, 31.0), (5.8, 28.5), (6.6, 29.0).

Perform a regression analysis and determine the PER.

**Solution:**

The sum and sums of squares of the x and y are  $\Sigma x = 62.2$ ;  $\Sigma x^2 = 307.00$ ;  $\Sigma y = 408.2$ ;  $\Sigma y^2 = 9138.62$ ;  $\Sigma xy = 1568.28$ ;  $N = 20$ . The mean of x =  $\Sigma x/N = 62.2/20 = 3.11$ .

$$a = \frac{408.2 - (62.2)(408.2/20)}{307.00 - (62.20)^2/20} = 2.631$$

$$b = \left(\frac{1}{20}\right) \left[ \frac{(408.20)(307.00) - (62.20)(1568.28)}{307.00 - (62.20)^2/20} \right] = 12.23$$

The mean of y =  $\Sigma y/N = 408.2/20 = 20.41$ . Thus the best-fit line will go through the point (3.11, 20.41).

The correlation coefficient “r” is calculated as follows:

$$r = \frac{20(1568.28) - 62.2(408.20)}{[[20(307.00) - (62.20)^2][20(9138.62) - (408.20)^2]]^{0.5}}$$

$$r = 0.9868$$

The correlation coefficient is very close to 1.0, indicating very good fit of the data to the regression equation. The regression and graphing can also be performed using a spreadsheet as discussed later in this chapter. The PER is the slope of the line, 2.631.

**1.1.5 Nonlinear Equations**

Nonlinear monovariate equations are those where the exponent of any variable in the equation is a number other than one. The polynomial:  $y = a + bx + cx^2 + dx^3$  is often used to represent experimental data. The term with the exponent 1 is the linear term, that with the exponent 2 is the quadratic term, and that with the exponent 3 is the cubic term. Thus b, c, and d are often referred to as the linear, quadratic, and cubic coefficients, respectively. Linear regression analysis is used to determine the coefficients of a polynomial that fits the experimental data. Although the polynomial is nonlinear, linear regression analysis is used because the first partial derivative of the function with respect to any of the coefficients is a constant. The objective of polynomial regression is to determine the coefficients of the polynomial such that the sum of the squares of the difference between experimental and predicted value of the response variable is a minimum. Polynomial regression is more difficult to perform manually than linear regression because of the number of coefficients that must be evaluated. Stepwise regression analysis may be performed, that is, additional terms are added to the polynomial, and the contribution of each additional term in reducing the error sum of squares is evaluated. To illustrate the complexity of polynomial compared with linear regression, the equations that must be solved to determine the coefficients are as follows:

For linear regression,  $y = ax + b$ :

$$\Sigma y = aN + b\Sigma x$$

$$\Sigma xy = aN \Sigma x + b\Sigma x^2$$

For a second-order polynomial,  $y = a + bx + cx^2$ :

$$\Sigma y = aN + b\Sigma x + c\Sigma x^2$$

$$\Sigma xy = aN\Sigma x + b\Sigma x^2 + c\Sigma x^3$$

$$\Sigma x^2y = aN\Sigma x^2 + b\Sigma x^3 + c\Sigma x^4$$

Thus, evaluation of coefficients for the linear regression is relatively easy, involving the solution of two simultaneous equations. On the other hand, polynomial regression involves solving  $n + 1$  simultaneous equations to evaluate coefficients of an  $n$ th order polynomial. Determinants can be used to determine the constants for an  $n$ th order polynomial. Techniques for solving determinants manually and using a spreadsheet program are discussed later in this chapter. For the second-order polynomial (quadratic) equation, the constants  $a$ ,  $b$ , and  $c$  are solved by substituting the values of  $N$ ,  $\Sigma x$ ,  $\Sigma x^2$ ,  $\Sigma x^3$ ,  $\Sigma x^4$ ,  $\Sigma xy$ , and  $\Sigma x^2y$ , into the three equations above and solving them simultaneously.

## 1.2 LINEARIZATION OF NONLINEAR EQUATIONS

Nonlinear equations may be linearized by series expansion, but the technique is only an approximation and the result is good only for a limited range of values for the variables. Another technique for linearization involves mathematical manipulation of the function and transformation and/or grouping such that the transformed function assumes the form:

$$F(x, y) = aG(x, y) + b$$

where  $a$  and  $b$  are constants whose values do not depend on  $x$  and  $y$ .

**Example 1.2.**  $xy = 5$ .

$$\text{Linearized form: } y = 5 \left( \frac{1}{x} \right)$$

A plot of  $y$  against  $(1/x)$  will be linear.

**Example 1.3.**

$$y = (y^2/x) + 4.$$

$$y^2 = xy - 4x \quad y^2 = x(y - 4) \quad \text{A plot of } x$$

against  $y^2/(y - 4)$  will be linear

**Example 1.4.** The hyperbolic function  $y = 1/(b + x)$ .

$$\frac{1}{y} = b + x$$

A plot of  $1/y$  against  $x$  will be linear.

**Example 1.5.** The exponential function  $y = ab^x$ .

$$\log y = \log a + x \log b$$

A plot of  $\log y$  against  $x$  will be linear.

**Example 1.6.** The geometric function  $y = ax^b$ .

$$\log y = \log a + b \log x$$

A plot of  $\log y$  against  $\log x$  will be linear.

### 1.3 NONLINEAR CURVE FITTING

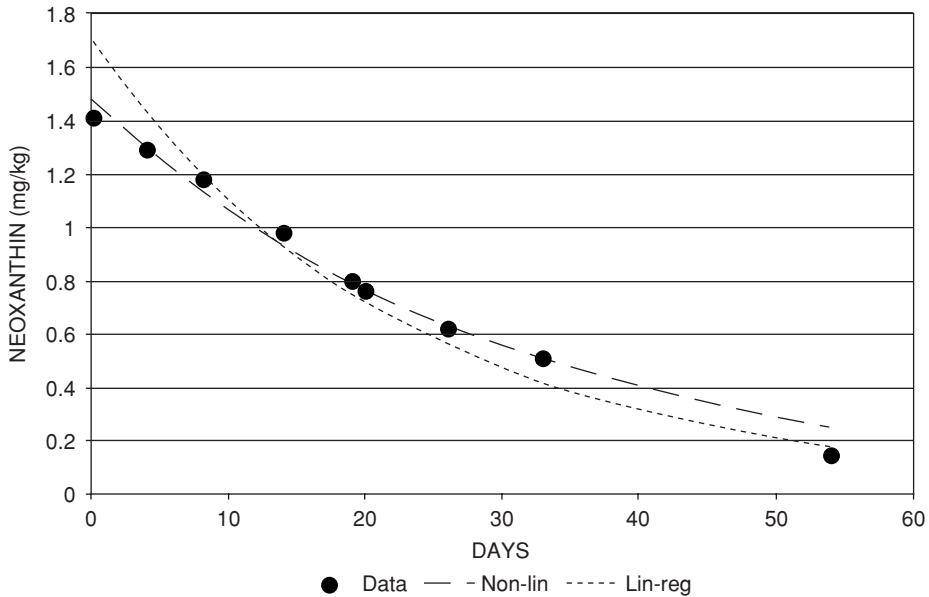
Linearizing an equation and fitting the linearized equation to the data has the advantage of simplicity but will require several replicates of entire data sets in order to be able to obtain reliable estimates of confidence limits for the equation parameters. Linearization also introduces complex errors particularly when two measured variables both appear in a linearized term. Nonlinear curve-fitting techniques permits determination of parameter estimates and their confidence interval from a single data set consisting of numerous data points. There are several nonlinear curve-fitting routines available. One commonly used software is Systat. To use Systat for data analysis, the data must be entered or imported into a Systat worksheet and saved as a Systat file.

To use Systat, first access the program and open the Systat main menu. Select *Window* and on the pop-up menu, select *Worksheet*. Data may then be entered in the worksheet. The first row should be the variable's name, and the values are entered in the column corresponding to the variables. Data may then be saved by selecting *File* and *Save*. Exit the worksheet by choosing the "X" (exit) button and return to the Systat main menu. To use data files saved in the Systat directory, chose *Open* in the *Worksheet* menu. Enter the *Filename* with the *.sys* extension and chose *Edit*. The system will return to the Systat Main menu and the following message is displayed: "Welcome to Systat. Systat variables available to you are." If a printout of the confidence interval of the parameter estimates is desired, select *Data* in the main menu and select *Format* in the pop-up menu. Then select *Extended (Long)* and *OK* to get back to the main menu. The Systat toolbar then becomes active. Select *Stats* in the Systat Main menu and select *Nonlin* in the pop-up menu. Follow the prompts. First select *Loss Function* and enter Loss function that is to be minimized. Usually this will be the sum of squares of the value of the dependent variable and the estimate. Although the sum of squares is the default, sometimes the program does not do the required iterations if nothing is entered for the loss function. Then select *OK* and when the display returns to the Systat Main menu, select *Stats* again, select *Nonlin* in the pop-up menu, and select *Model*. Enter the model desired for fitting into the data. Enter initial values of the coefficients separated by commas. Enter number of iterations. Select *OK* and Systat will return values of the parameter estimates and the loss function.

**Example 1.7.** Data on degradation of neoaxanthin, a carotenoid pigment in olives [*J. Agric. Food Chem.* (1994) 42:1551–1554] is as follows [Days, Conc. (in mg/kg)]: (0, 1.41), (4, 1.29), (8, 1.18), (14, .98), (19, 0.80), (20, 0.76), (26, 0.62), (33, 0.51), (54, 0.13). The change of concentration with time is first order, therefore the logarithm of concentration when plotted against time is linear. Fit the logarithmic equation  $\ln(C) = kt + b$  by linear regression to obtain parameter estimates of  $k$  and  $b$ . Also fit the equation  $C = [e]^{kt+b}$  and obtain parameter estimates of  $k$  and  $b$  and their confidence limits using nonlinear curve fitting.

**Solution:**

Enter the data into the worksheet, save and exit. The Systat main menu will indicate that the following variables are available: "Days and Neo." Select *Data*, then *Format*, then *Extended (long)*, and *OK*.



**Figure 1.1** Graph showing fit to experimental data of a first-order equation with model parameters determined using linearization and linear regression (Lin-reg) and nonlinear curve fitting (Non-lin).

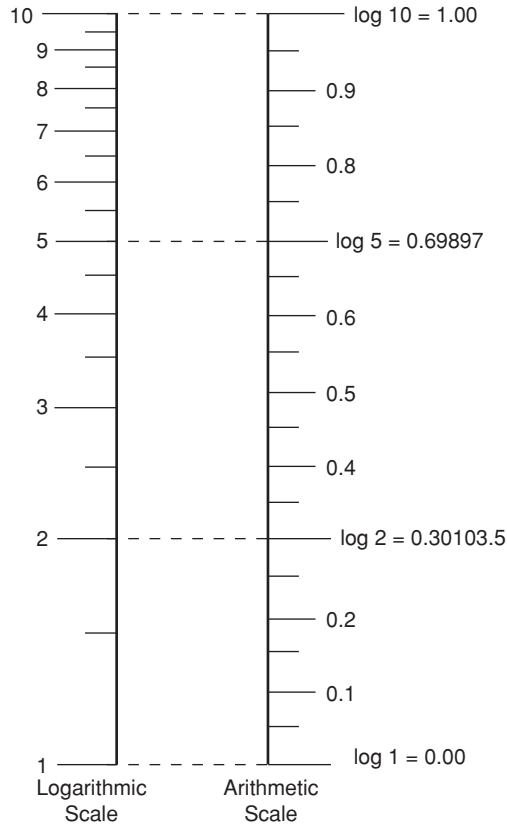
Back into the Systat main menu, select *Stats* then *Nonlin* and *Loss Function*. Enter “(Neo–estimate)<sup>2</sup>” in the loss function expression box and select *OK*. Back in the Systat main menu, select *Stats*, then *Nonlin*, then *Model*. Enter “neo = exp(k\*days + b)” in the *Model* expression box, –1, 1 in the *Start* box, and 20 in the *Iterations* box. Select *OK*. Parameter estimates  $k = -0.033 \forall .005$  and  $b = 0.387 \forall .066$  and a loss function of .023 are displayed. To ensure that this is not a local minimum for the loss function, select *Stats*, then *Nonlin*, then *Resume*. Enter –.1 and 0.5 in the *Start* box and 20 in the *Iterations* box. Select *OK*. Displayed values of  $k$  and  $b$  are the same as above.

To fit a linearized form of the first-order equation, use  $\ln(\text{neo}) = k \cdot \text{days} + b$ . Transform the values for concentration of neoxanthin into their natural logarithms and perform a linear regression. This may be done using the *Regrn* function of Systat or the Statistics routine in Excel. Using Systat, enter the values of  $\ln(\text{neo})$  at indicated days in the worksheet, and save. The Systat main menu then appears. Select *Regrn*. Select  $\ln(\text{neo})$  as the dependent and days as the independent variable. Select *OK*. Systat displays –0.043 as the slope and 0.521 as the constant. The correlation coefficient is 0.958 showing reasonably good fit of the linearized equation to the data.

Figure 1.1 shows a plot of the experimental data and the fitted equations. The nonlinear curve-fitted parameters show closer values to the experimental data than the linearized transformed variable fitted parameters. Linearization forced the function to be strongly influenced by the last data point resulting in underestimation of the middle and overestimation of the first few data points. Nonlinear curve fitting is recommended over linearization, when possible.

The solver feature of Microsoft Excel may also be used to do the curve fitting. An example of how Excel may be used for curve fitting to determine kinetic parameters is shown in the section “Determining Kinetic Parameters” in Chapter 8.



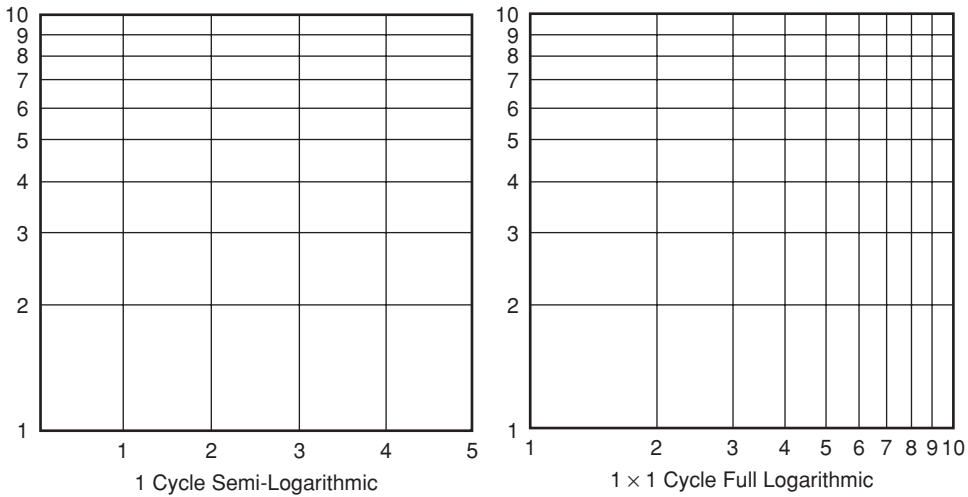


**Figure 1.2** Scaling of logarithmic scale used on the logarithmic axis of semi-logarithmic or full logarithmic graphing paper.

#### 1.4 LOGARITHMIC AND SEMI-LOGARITHMIC GRAPHS

Graphing paper is available in which the ordinate and abscissa are in the logarithmic scale. A full logarithmic or log-log graphing paper has both abscissa and ordinate in the logarithmic scale. A semi-logarithmic graphing paper has the ordinate in the logarithmic scale and the abscissa in the arithmetic scale. Full logarithmic graphs are used for geometric functions as in Example 1.6 above, and semi-logarithmic graphs are used for exponential functions as in Example 1.5. The distances used in marking coordinates of points in the logarithmic scale are shown in Fig. 1.2. Each cycle of the logarithmic scale is marked by numbers from 1 to 10. Distances are scaled on the basis of the logarithm of numbers to the base 10. Thus, there is a repeating cycle with multiples of 10. One cycle semi-logarithmic and full logarithmic graphing paper is shown in Fig. 1.3.

When plotting points on the logarithmic scale, label the extreme left and lower coordinates of the graph with the multiple of 10 immediately below the magnitude of the least coordinate to be graphed. Thus, if the least magnitude of the coordinate of the point to be plotted is 0.025, then the extreme left or lower coordinate of the graph should be labeled 0.01. The number of cycles on the logarithmic scale of the graph to be used must be selected such that the points plotted will occupy most of the graph



**Figure 1.3** One cycle semi-logarithmic and full logarithmic graphing paper.

after plotting. Thus, if the range of numbers to be plotted is from 0.025 to 3.02, three logarithmic cycles will be needed (0.01 to 0.1; 0.1 to 1; 1 to 10). If the range of numbers is from 1.2 to 9.5, only one cycle will be needed (1 to 10).

Numerical values of data points are directly plotted on the logarithmic axis. The scaling of the graph accounts for the logarithmic relationship. Thus, points, when read from the graph, will be in the original rather than the logarithmically transformed data.

$$\text{Slope} = \frac{\log y_2 - \log y_1}{\log x_2 - \log x_1}$$

Slopes on log-log graphs are determined using the following formula:

Coordinates of points  $(x_1, y_1)$  and  $(x_2, y_2)$ , which are exactly on the line drawn to best fit the data points, are located. Enough separation should be provided between the points to minimize errors. At least one log cycle separation should be allowed on either the ordinate or abscissa between the two points selected.

Slopes on semi-logarithmic graphs are calculated according to the following formula:

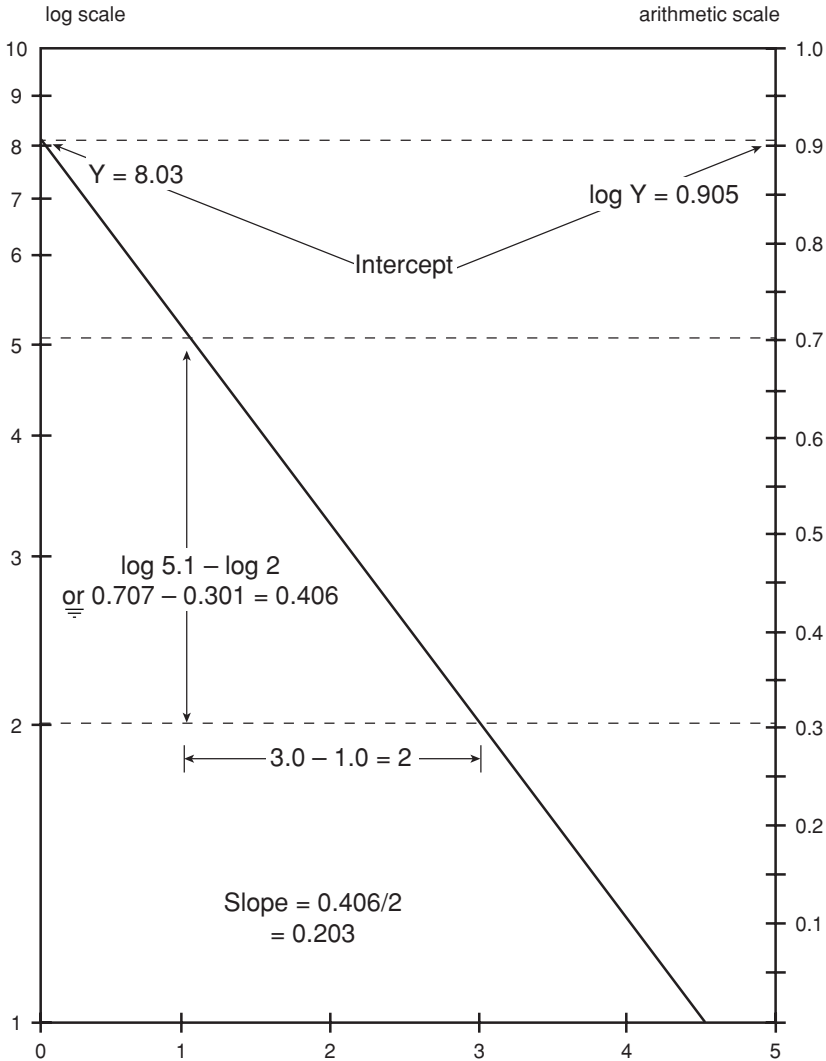
$$\text{Slope} = \frac{\log y_2 - \log y_1}{x_2 - x_1}$$

A separation of at least one log cycle, if possible, should be allowed between the points  $(x_1, y_1)$  and  $(x_2, y_2)$ . Figure 1.4 shows the logarithmic scale relative to the arithmetic scale that would be used if the data is transformed to logarithms prior to plotting. The determination of the slope and intercept is also shown.

The following examples illustrate the use of semi-log and log-log graphs:

**Example 1.8.** An index of the rate of growth of microorganisms is the generation time ( $g$ ). In the logarithmic phase of microbial growth, number of organisms ( $N$ ) change with time of growth ( $t$ ) according to:

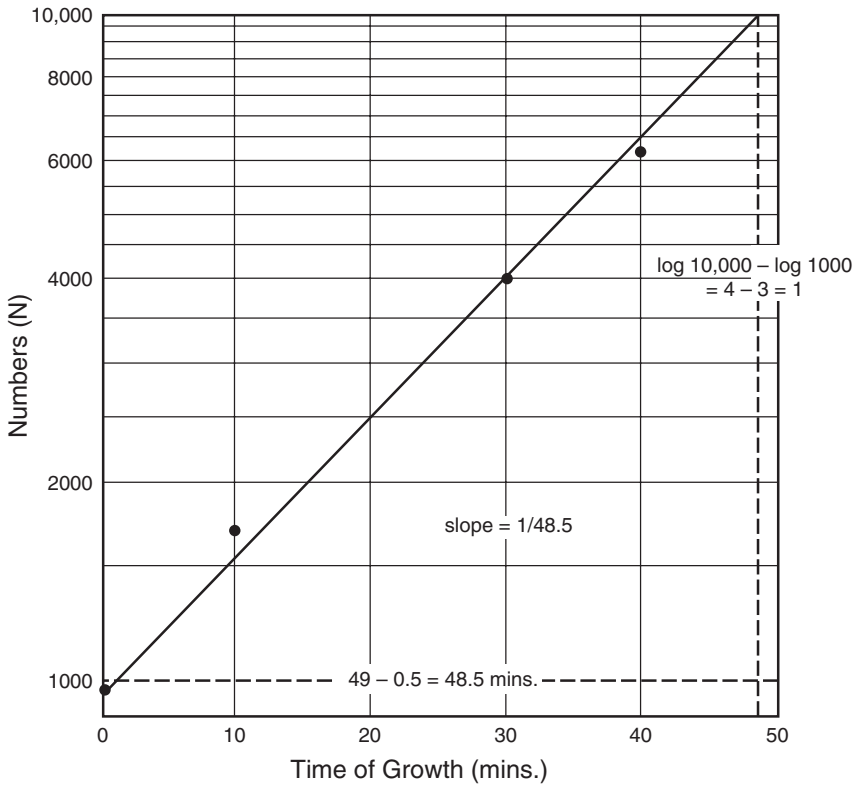
$$N = N_0[2]^{t/g}$$



**Figure 1.4** Graph showing the logarithmic relative to the arithmetic scale, and how the slope and intercept are determined on a semi-logarithmic graph.

Find the generation time of a bacterial culture that shows the following numbers with time of growth:

<i>Numbers (N)</i>	<i>Time of growth, (t), in minutes</i>
980	0
1700	10
4000	30
6200	40



**Figure 1.5** Semi-logarithmic plot of microbial growth.

**Solution:**

Taking the logarithm of the equation for cell numbers as a function of time:

$$\text{Slope} = \frac{\log 2}{g}$$

$$\log N = \log N_0 + (t/g) \log 2$$

Plotting log N against t will give a straight line. A semi-logarithmic graphing paper is required for plotting. The slope of the line will be from Fig. 5, the two points selected to obtain the slope are (0,1000) and (48.5,10000). The two points are separated by one log cycle on the ordinate. The slope is  $1/48.5 = 0.0206 \text{ min}^{-1}$ . The generation time  $g = \log 2/\text{slope} = 14.6$  minutes.

Regression eliminates the guesswork in locating the position of the best-fit line among the data points. Let  $\log(N) = y$  and  $t = x$ . The sums are  $\Sigma x = 80$ ,  $\Sigma y = 13.616$ ,  $\Sigma x^2 = 2600$ ,  $\Sigma y^2 = 46.740$ ,  $\Sigma xy = 292.06$ .

$$a = \frac{292.06 - 80(13.616)/4}{2600 - (80)^2/4} = 0.01974$$

$$b = \frac{13.616(2600) - 80(292.06)}{4[2600 - (80)^2/4]} = 3.0092$$

The graph is shown in Fig. 1.5. A best-fit line is drawn by positioning the straight edge such that points below the line balance those above the line. Although the equation for  $N$  suggests that any two data points may be used to determine  $g$ , it is advisable to plot the data to make sure that the two points selected lie exactly on the best-fitting line.

The correlation coefficient is:

$$r = \frac{4(292.06 - 80(13.616))}{([4(2600) - (80)^2][4(46.740) - (13.616)^2])^{0.5}} = 0.9981$$

The correlation coefficient is very close to 1.0, indicating good fit of the data to the regression equation. The slope is 0.01974.  $g = \log(2)/0.01974 = 15.2$  minutes.

The parameter estimate for  $g$  by nonlinear curve fitting using Systat and the model  $[N = 980 \cdot 10^{-(\text{time}/g)]$  returns a parameter estimate for  $g$  of  $14.834 \pm 0.997$ .

**Example 1.9.** The term “half-life” is an index used to express stability of a compound and is defined as the time required for the concentration to drop to half the original value. In equation form:

$$C = C_0[2]^{-t/t_{0.5}}$$

where  $C_0$  is concentration at  $t = 0$ ,  $C$  is concentration at any time  $t$ , and  $t_{0.5}$  is the half-life.

Ascorbic acid in canned orange juice has a half-life of 30 weeks. If the concentration just after canning is 60 mg/100 mL, calculate the concentration after 10 weeks. When labeling the product, the concentration declared on the label must be at least 90% of the actual concentration. What concentration must be declared on the label to meet this requirement at 10 weeks of storage?

### Graphical Solution:

A logarithmic transformation of the equation for concentration as a function of time results in:

$$\log C = \log C_0 - \left[ \frac{\log 2}{t_{0.5}} \right] t$$

A plot of  $C$  against  $t$  on semi-logarithmic graphing paper will be linear with a slope of  $-(\log 2)/t_{0.5}$ .

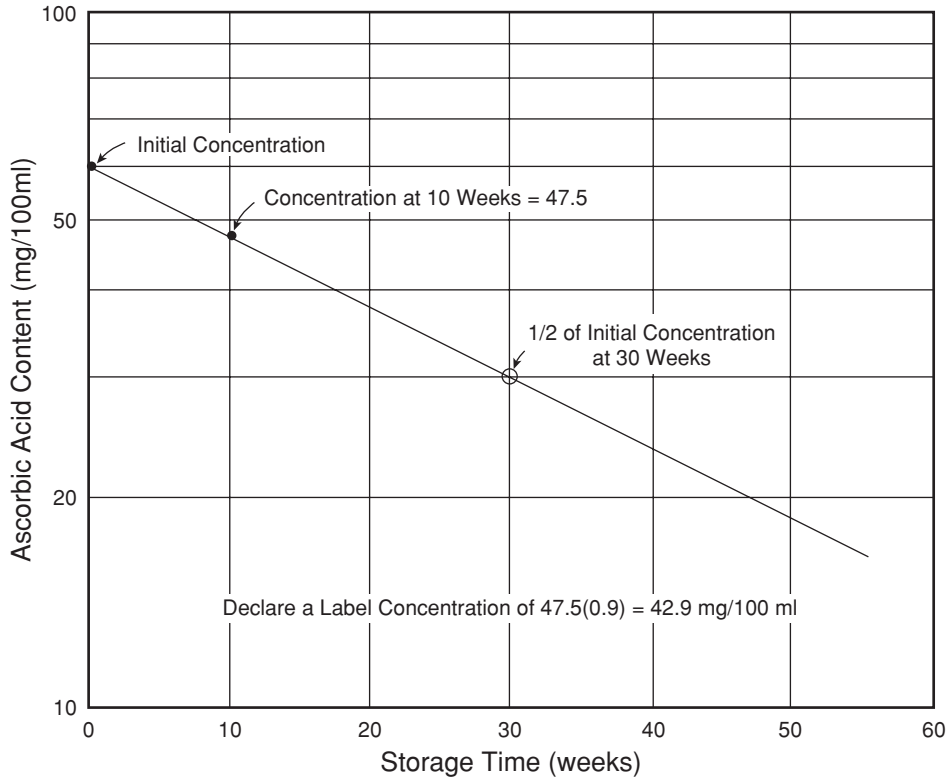
Figure 1.6 is a graph constructed by plotting 60 mg/100 mL at  $t = 0$  and half that concentration (30 mg/100 mL) at  $t = 30$  weeks and drawing a line connecting the two points. At  $t = 10$  weeks, a point on the line shows a concentration of 47.5 mg/100 mL. Thus, a concentration of  $0.9(47.5)$  or 42.9 mg/100 mL would be the maximum that can be declared on the label.

### Analytical Solution:

Given:  $C_0 = 60$ ;  $t_{0.5} = 30$ ; at  $t = 10$ ,  $C_{10}$  = concentration and the declared concentration on the label,  $C_d = 0.9 C_{10}$ . Solving for  $C_d$ :

$$\begin{aligned} C_d &= 0.9(60)[2]^{-10/30} \\ &= 0.9(60)(0.7938) = 42.86 \text{ mg/mL} \end{aligned}$$

**Example 1.10.** The pressure-volume relationship that exists during adiabatic compression of a real gas is given by  $PV^n = C$ , where  $P$  is absolute pressure,  $V$  is volume,  $n$  is the adiabatic expansion factor,



**Figure 1.6** Graphical representation of the half-life illustrated by ascorbic acid degradation with time of storage.

and  $C$  is a constant. Calculate the value of the adiabatic expansion factor,  $n$ , for a gas that exhibits the following pressure-volume relationship:

Volume (ft <sup>3</sup> )	Absolute Pressure (lb <sub>f</sub> /in. <sup>2</sup> )
53.3	61.2
61.8	49.5
72.4	37.6
88.7	28.4
118.6	19.2
194.0	10.1

**Solution:**

The equation may be linearized and the value of  $n$  determined from the linear plot of the data. Taking the logarithm:

$$\log P = -n \log V + \log C$$