

APPLIED MATHEMATICS IN CHEMICAL ENGINEERING

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PREFACE

Applied mathematics has assumed increasing importance to the chemical engineer. The authors of current professional literature freely use transform, vector, and finite-difference methods to attack a problem. The practicing engineer is finding modern mathematical techniques a valuable tool in the analysis of a variety of situations. Present trends in the chemical and process industries involve increased emphasis on automatic-control systems, high-speed machine computation, operational analysis, and the like. These developments directly depend upon the application of advanced mathematical procedures.

The purpose of this book is to consolidate the advanced methods of mathematics into a form that can be applied readily by both the student and the professional engineer. Emphasis is focused on the engineering applications of mathematics. Considerable attention is given to the problem of expressing a physical situation in mathematical language. Problems drawn from the engineering literature are used to illustrate the mathematical procedures. The material covered falls into three broad categories: (1) the treatment and interpretation of engineering data, (2) the analysis of situations involving only one independent variable, and (3) the analysis of situations involving two or more independent variables.

The mathematical background of the reader is presumed to be limited. The text material begins with a discussion of the process of differentiation, and the development of more advanced procedures follows in a step-by-step manner.

The book may be used as either an undergraduate or a graduate text. The material of Chaps. 1, 3, 4, and 5 can be handled readily by the undergraduate and will provide the background needed for the assimilation of the more advanced material in a subsequent study program.

The second edition represents an extensive revision of the original work. Chapter 8 (The Laplace Transform), Chap. 9 (Analysis of Stagewise Processes by the Calculus of Finite Differences), and Chap. 10 (The Numerical Solution of Partial Differential Equations) are completely new. The remaining chapters have been rewritten, and new material has been

added. Such topics as the statistics of small samples, analysis of variance, factorial design of experiments, expansion in a series of orthogonal functions, vector notation, and others have been included.

The decision to add new material and to omit material formerly included has been difficult. The action taken has been based upon an appraisal of trends both in engineering education and in the engineering profession.

The authors are indebted to Professor Sir Ronald A. Fisher, Cambridge, and to Oliver & Boyd, Ltd., Edinburgh and London, for permission to reprint Table 2-1 from their book "Statistical Methods for Research Workers"; to Professor P. C. Mahalanobis, F.R.S., Calcutta, and to the Indian Statistical Institute, Calcutta, for permission to reprint Table 2-4 from an article appearing in *Sankhyā*; to Professor G. W. Snedecor, Ames, Iowa, and to Collegiate Press, Inc., of Iowa State College, Ames, for permission to reprint Table 2-5 from their book "Statistical Methods Applied to Experiments in Agriculture and Biology"; to Professor R. V. Churchill, Ann Arbor, Mich., and to McGraw-Hill Book Company, Inc., New York, for permission to reprint Table 8-1 from their book "Modern Operational Mathematics in Engineering." The constructive suggestions and encouragement of the author's professional colleagues are gratefully acknowledged. In particular, the invaluable aid in the preparation of the second edition by the authors of the first edition, Professor T. K. Sherwood and Dr. C. E. Reed, is sincerely appreciated.

HAROLD S. MICKLEY

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CHAPTER 1

TREATMENT OF ENGINEERING DATA

1-1. Introduction. The engineer constantly utilizes experimental data. He tests theoretical predictions by comparison with experiment; he analyzes process performance by examination of experimental results; he makes critical decisions on the basis of his interpretation of experimental measurements. Consequently, the ability to extract maximum information from engineering data is important. This chapter discusses several useful techniques for the treatment of experimental results.

1-2. Graphical Representation. Graphical methods have proved invaluable in the analysis of the relatively complex processes with which the chemical engineer deals. Much of the basic physical and chemical data are best represented graphically, and graphical methods are introduced in this way into the analytical treatment of the process.

One or more of the many types of graphical representations may be employed for the following purposes: (1) as an aid in visualizing a process or the meaning of a computation, (2) for the representation of quantitative data or of a theoretical or empirical equation, (3) for the comparison of experimental data with a theoretical or empirical expression, and (4) as a means of computation.

The relation between two physical quantities p and x is commonly obtained as a tabulation of values of p for a number of different values of x . The relation between p and x is not easy to visualize by studying the tabulated results and is best seen by plotting p vs. x . If the conditions of the experiment are such that p is known to be a function of x only, the functional relation will be indicated by the fact that the points may be represented graphically by a smooth curve, and deviations of the points from a smooth curve indicate the reliability of the data. If p is a function of two variables x and y , a series of results of p in terms of x may be obtained for each of several values of y . When plotted, the data will be represented by a family of curves, each curve representing the relation between p and x for a definite constant value of y . If another variable z is involved, we may have separate graphs for constant values of z , each showing a family of curves of p vs. x . Extension of this method of representing data to relate more than four quantities is

impractical unless general relations between two or more of the variables can be obtained. This point is further discussed below.

The ordinary graphical representation of experimental results is usually the first step in finding an empirical equation to represent the data, as described in Sec. 1-5. Even when the empirical equation is to be obtained directly from the tabulated data by a numerical process, it is usually desirable to plot the points in order that the nature of the function may be visualized. Where the calculated relation between two quantities is dependent wholly on sound theoretical or empirical equations, it may be desirable to plot the resulting function in order to visualize its properties.

The use to which the graph is to be adapted should be kept in mind in preparing a graphical representation either of data or of an equation. The coordinates should be chosen in such a way that the accuracy of reading the graph will be good for all ranges of the variables involved, with the resulting curve falling with a slope of roughly ± 1 on a square diagram. The scale should be arranged so that interpolation is readily accomplished.

Consider the relation

$$E = \frac{8}{\pi^2} \left\{ \exp \left[- \left(\frac{\pi}{2} \right)^2 \tau \right] + \frac{1}{9} \exp \left[- 9 \left(\frac{\pi}{2} \right)^2 \tau \right] + \frac{1}{25} \exp \left[- 25 \left(\frac{\pi}{2} \right)^2 \tau \right] + \cdots \right\} \quad (1-1)$$

which is obtained as the analytical solution to the problem of the un-

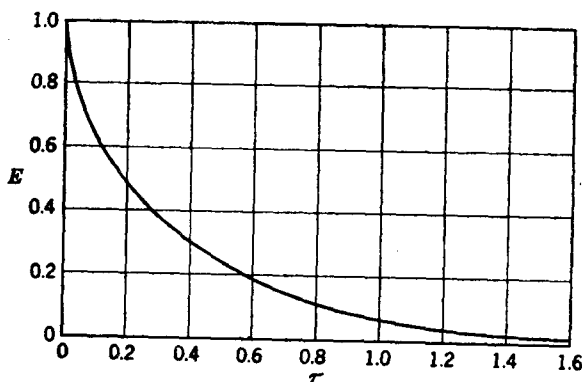


FIG. 1-1. Linear-scale plot of E - τ function.

steady-state cooling of an infinite solid slab. Values of E may be obtained directly for any value of τ , but a tedious trial-and-error calculation is necessary if τ is to be obtained for a given value of E . By means of a graph of E vs. τ , E may be read in terms of τ or τ in terms of E with equal facility.

Figure 1-1 shows E plotted vs. τ on ordinary rectangular coordinate paper. It is apparent that τ cannot be read accurately for large values of E , nor can E be obtained accurately at large values of τ . When τ is large, the first term of the series is the only one of significance, and the series reduces to an exponential relation, suggesting a graph of $\log E$ vs. τ .

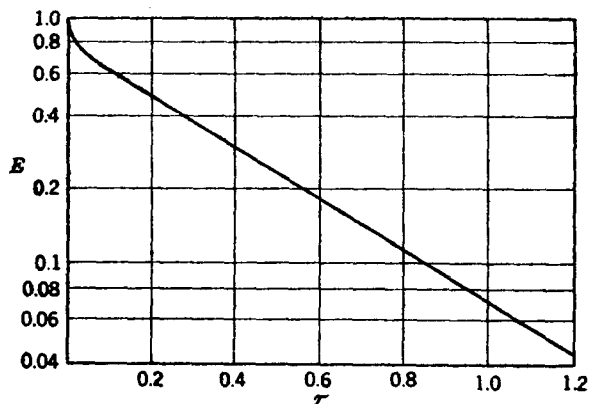


FIG. 1-2. Semilog plot of E - τ function.

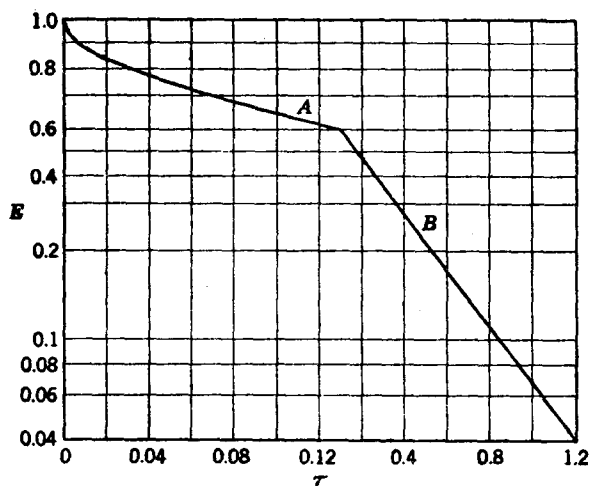


FIG. 1-3. Extended abscissa scale.

or a graph of E vs. τ on semilogarithmic coordinate paper. Figure 1-2 is such a graph of E vs. τ , with a logarithmic ordinate scale and a linear abscissa scale. It is apparent that this method of plotting represents a considerable improvement, as the graph may be read with good accuracy (in view of its size) except for small values of τ . Figure 1-3 represents a further modification of the same graph. The logarithmic scale from

$E = 0.6$ to $E = 1.0$ has been doubled and a larger abscissa scale used in this region. The result is a combination of two graphs similar to Fig. 1-2, with different ordinate and abscissa scales for values of E greater and less than 0.6. The two graphs are fitted together, giving a curve with two branches. The accuracy in reading values from branch *A* is considerably improved, although the accuracy at large values of τ is less than in Fig. 1-2.

1-3. Elimination of Trial and Error. Experimental data or correlations of experimental data should be plotted, if possible, so that the use of the graph should eliminate trial-and-error calculations. This is not

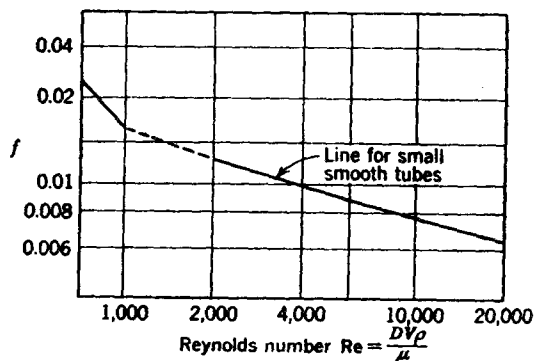


FIG. 1-4. Friction-factor-Reynolds-number plot.

always possible for all uses to which the graph may be adapted, but alternative methods of plotting may be used to advantage in employing the data in different ways. The familiar friction-factor graph for fluids in round pipes represents a correlation of a large amount of data, usually plotted as f vs. $DV\rho/\mu$ with logarithmic ordinate and abscissa scales (Fig. 1-4). This is used in connection with the Fanning equation

$$H = \frac{2fLV^2}{g_c D} \quad (1-2)$$

where H = head lost because of friction in length L of pipe having diameter D

g_c = "consistency factor"

V = superficial fluid velocity

ρ = fluid density

μ = fluid viscosity

f = dimensionless friction factor

When all quantities are known except the head loss H , which is to be calculated, the group Re is first obtained, f is read from the plot, and H is calculated directly from the equation. If it is desired to calculate

the necessary pipe diameter for a specified flow and head, the problem becomes one of trial and error, since the Reynolds group is not immediately obtainable. Similarly, trial and error are involved in the calculation of the flow to be expected with a specified head, fluid, and pipe size. It is clear that the method of plotting is inconvenient for two of the three usual calculations in connection with which the correlation is of value. The following procedure will determine the manner in which the graphed data should be replotted in order to eliminate trial and error in a specific type of calculation.

Consider the case in which it is desired to calculate the pipe diameter corresponding to a specified flow and head. What is needed is a plot prepared by using Fig. 1-4, in which the abscissa contains only known quantities and the ordinate the unknown (and any necessary known) parameters.

Let Q represent the given volume rate of flow. Then the relations which are available are Eq. (1-2),

$$Q = \frac{\pi}{4} D^2 V \quad (1-3)$$

$$\text{Re} = \frac{DV\rho}{\mu} \quad (1-4)$$

and the relation between f and Re given by Fig. 1-4. The "unknowns" are four in number: D , V , Re , and f . There are four "equations" (one of them graphical) and four unknowns, and so a solution is possible. The algebraical relations are used to eliminate those unknowns which do not appear directly in the graph, in this case, D and V . Combination of (1-3) and (1-4) gives

$$V = \frac{\pi(\text{Re})^2\mu^2}{4Q\rho^2} \quad (1-5)$$

$$D = \frac{4Q\rho}{\pi(\text{Re})\mu} \quad (1-6)$$

Substitution of (1-5) and (1-6) in (1-2) gives

$$\text{Re} \sqrt[5]{f} = \left(\frac{32g_c}{\pi} \right)^{1/5} \left(\frac{H}{L} \right)^{1/5} \frac{Q\rho}{\mu} \quad (1-7)$$

The right-hand side of Eq. (1-7) contains known quantities only. Furthermore, Fig. 1-4 may be used to prepare a plot of $\text{Re} \sqrt[5]{f}$ vs. either f or Re . With the aid of such a plot, Re or f may be obtained, without trial and error, from the specified data. Equations (1-5) to (1-7) may then be used to calculate the remaining variables.

A graph of $Re \sqrt{f}$ vs. Re is shown in Fig. 1-5. Since Re appears in both variables plotted, the calculated value of D is quite insensitive to f . This is true because of the relation between the variables and not because of the method of plotting, although it will be shown below that graphical representations of data should not, in general, involve the same variable in both ordinate and abscissa.

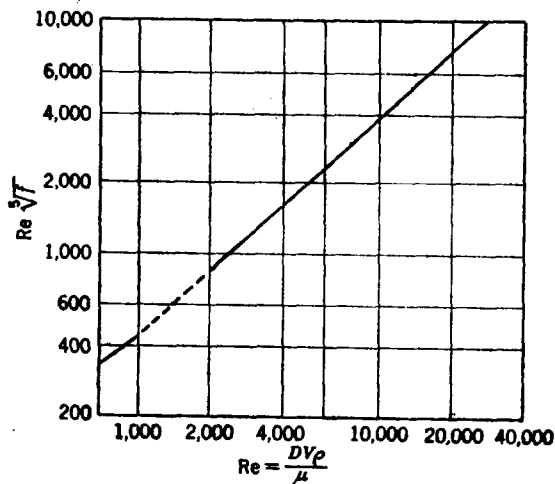


FIG. 1-5. Modified friction-factor plot.

Following the same principle of eliminating the variable to be determined from one of the quantities plotted, it may be shown that the third calculation to determine the flow for a specified head and pipe size is easily carried out, using a plot of $Re \sqrt{f}$ vs. Re or f .

1-4. Misleading Methods of Correlation. Any correlation of experimental data based on a graph in which the same variable appears in both ordinate and abscissa should be viewed with suspicion. When one of the less important variables is placed in both quantities plotted, it is possible to extend the scale and make the correlation appear to be much better than it really is. Such correlations are occasionally presented in the literature. The investigator, trying various methods of plotting his results, hits upon a method of plotting that brings his data together and presents a correlation that is unintentionally deceiving as to its generality. Such methods of plotting may be arrived at by fairly sound analysis of the physical problem involved and may be defended as being rational, although a poor test of the data. A rather subtle example of this process arises in the study of heat transfer to boiling liquids. The surface coefficients obtained are large and are relatively difficult to reproduce, so that the problem of correlating such data is

difficult. Suppose a set of data to have been obtained, covering a range of temperature differences between steam and boiling water in an evaporator relying on liquid circulation by natural convection. The experimenter is confronted with a series of values of h and Δt , all the results having been obtained with a constant liquid composition and boiling

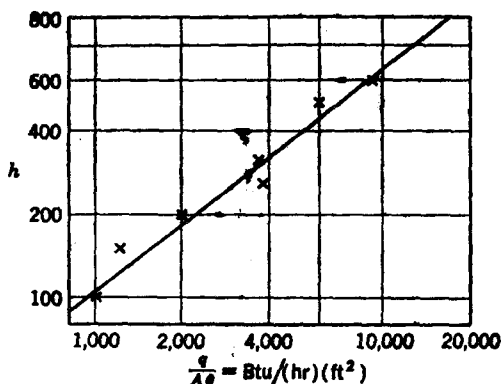


Fig. 1-6. Correlation of data on heat transfer.

temperature. He reasons that the surface coefficient of heat transfer is dependent on the effective thickness of some type of surface film and that this in turn should be a function of the degree of agitation of the liquid in the evaporator. The agitation should be a function of the rate of boiling and the rate of heat transfer, in turn. He reaches the conclusion, therefore, that h should depend on the heat "current density" $q/A\theta$ and prepares a graph to test this conclusion. The result is shown in Fig. 1-6, which indicates a better correlation than is often obtained for this case of heat transfer.

It should be noted, however, that the abscissa $q/A\theta$ is the calculated product of h and Δt , and the graph, therefore, involves h in both ordinate and abscissa. If h is plotted vs. Δt , the result indicates a poor correlation

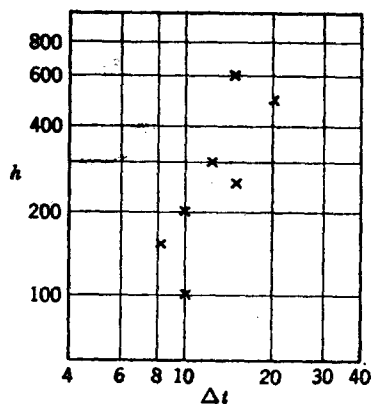


Fig. 1-7. Test of boiling heat-transfer data.

of the same data, as shown by Fig. 1-7. Fundamentally, the two graphs, Figs. 1-6 and 1-7, are equivalent, but the former appears to present a better correlation of the data because large variations in h overshadow small deviations of Δt . It may be argued that the quantities varied were the rate of heat flow and the steam temperature and that these

should be the variables plotted, but general correlations on such a basis would be inconvenient, and the graph of h vs. Δt is an excellent test of the experimental data.

From the example quoted above, it follows that if one variable plotted is *divided* by some function of the other, a graph of the resulting ratio may present a more severe test of the data. For example, fluid-flow data are frequently plotted as

$$f = \frac{\pi^2 H g_c D^5}{32 L Q^2}$$

vs.

$$\text{Re} = \frac{4 Q \rho}{\pi \mu D}$$

If the experimental variables are H and D , with L , Q , μ , and ρ held constant, the graph of f vs. Re is really a graph of $H D^5$ vs. $1/D$. If the measured value of D is 10 per cent too great but H is correct, the abscissa will be 9 per cent too small, and the ordinate will be 61 per cent high. The general slope of the curve is negative, and the experimental point will be considerably off. In this case, the method of plotting represents a severe test of the data. If the experimental variables are H and ρ , all others being held constant, then the usual friction-factor graph represents a direct plotting of the variables studied. When a number of variables are to be related, it is seldom possible to find a single method of plotting that will represent an equally critical test of the experimental data relating various pairs of the variables.

1-5. Empirical Equations. The representation of experimental data by means of algebraic equations is a practical necessity in engineering. Not only are such equations shorthand expressions for a large amount of data, but they serve as the necessary mathematical expressions by which the empirical information may be treated in subsequent mathematical operations. For the first use, the equation must be truly representative of the experimental data; for the second, it should be simple in form.

The form of the equation is frequently suggested by a theoretical analysis, and it is necessary only to evaluate certain constants. If the form is not known, dimensional analysis may be helpful in suggesting grouping of variables, and obvious practical considerations must not be overlooked. It is often evident that the curve must go through the origin or some fixed point or perhaps become asymptotic to some definite value of one variable. The form of the empirical equation chosen must be consistent with such considerations. The general problem of fitting data by an empirical equation may be divided into two parts: the determination of a suitable form of equation and the evaluation of the constants. The determination of the form proceeds largely by trial, although certain rules may be laid down as practical aids. If the data

can be plotted in such a way as to give a straight line, either by choice of graph paper or by a proper arrangement of variables for plotting, the linear form leads immediately to an expression relating the original variables. Likely forms are tested by plotting in such a manner as to make the expression linear, and the constants are evaluated from the straight line obtained.

The experimental data may be assumed to be given in the form of a table of values of a variable y for corresponding values of another variable x . For example, let it be desired to represent the following data by means of an empirical equation:

x	0.2	0.5	1.0	2.0	3.0	4.0
y	3.2	3.7	4.1	8.1	13.7	22.6

To make the problem general, it will be assumed that there is no additional information as to the nature of the function.

The data may always be represented by a trigonometric series or by a polynomial having a sufficient number of terms; the six points tabulated may be represented by a polynomial of the fifth degree, containing six arbitrary constants. A form involving so many constants is undesirable for three reasons: The constants would be quite difficult to evaluate; the expression obtained would be relatively complicated to use; and the determinations presumably involve experimental errors of such magnitude that an approximate representation is all that is justified. The problem, therefore, is to represent the data by an expression of the simplest possible form that fits the tabulated results within the estimated experimental error.

The first thing to do is to plot the data on ordinary rectangular coordinates, as shown in Fig. 1-8. This serves two purposes: The nature of the function is easily visualized, so that the empirical form to be employed may be more readily selected; and the possibility of the simple linear form

$$y = a + bx \quad (1-8)$$

is tested at the outset. The points do not fall on a straight line in Fig. 1-8, and the simple linear form is not applicable. Usually, the next thing to do is to plot the data on logarithmic paper in order to test the form

$$y = ax^n \quad (1-9)$$

This form is very often applicable and is not too complicated for ordinary use. It is represented by a straight line of y vs. x on logarithmic paper, having a slope n and an "intercept" a at $x = 1$. If the ordinate and abscissa scales are equal, i.e., if the distances along the axes are the same