Mathematical Methods in Chemical Engineering

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PREFACE

THE development of new processes in the chemical industry is becoming more complex and increasingly expensive. If the research and development of the process can be carried out with confidence, the ultimate design will be more exact, and therefore the plant will operate more economically. In all facets of such a project, mathematics, which is the language of the quantitative, plays a vital role. Therefore training in mathematical methods is of the utmost importance to chemical engineers. The present text has been written with these ideas in mind, and we would emphasize that our aim is to present mathematics in a form suitable for the engineer rather than to teach engineering to mathematicians. To the pure mathematician an elegant proof is an end in itself, but to the chemical engineer it is merely a means to an end. Consequently this book only sketches demonstrations of the validity of theorems, to encourage the reader to have more confidence in the use of the technique for the solution of engineering problems. In addition, an attempt has been made to sort out the useful from the trivial and flamboyant of the wide variety of mathematical techniques available.

The material presented in this book is based on various undergraduate and post graduate courses given in the Chemical Engineering Department of the University of Birmingham. Many of the worked examples have been selected from research work carried out in the department, and these are supplemented with problems taken from the chemical engineering literature. Some chapters of the book (notably Chapters 4 and 5) are almost entirely mathematical, but wherever possible the text has been illustrated with chemical engineering applications.

The book was written when both authors were lecturers in the Chemical Engineering Department of the University of Birmingham. It is hoped that the text will encourage chemical engineers to make greater use of mathe-

matics in the solution of their problems.

We wish to express our thanks to Professor J. T. Davies for initiating the venture, and to Professor F. H. Garner, and Professor S. R. M. Ellis for their interest and advice in the preparation of the text.

Birmingham July, 1963

V.G.J. and G.V.J.

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M.M.C.E.

THE MATHEMATICAL STATEMENT OF THE PROBLEM

1.1. Introduction

NEARLY all applied science consists of performing experiments and interpreting the results. This may be done quantitatively by taking accurate measurements of the system variables which are subsequently analysed and correlated, or qualitatively by investigating the general behaviour of the system in terms of one variable influencing another. The first method is always desirable, and if a quantitative investigation is to be attempted it is better to introduce the mathematical principles at the earliest possible stage, since they may influence the course of the investigation. This is done by looking for an idealized mathematical model of the system.

The second step is the collection of all relevant physical information in the form of conservation laws and rate equations. The conservation laws of chemical engineering are material balances, heat balances, and other energy balances; whilst the rate equations express the relationship between flow rate and driving force in the fields of fluid flow, heat transfer, and diffusion of matter. These are then applied to the model, and the result should be a mathematical equation which describes the system.

The type of equation (algebraic, differential, finite difference, etc.) will depend upon both the system under investigation, and the detail of its model. For a particular system, if the model is simple the equation may be elementary, whereas if the model is more refined the equation will be a more difficult type. The appropriate mathematical techniques are then applied to this equation and a result is obtained. This mathematical result must then be interpreted through the original model in order to give it a physical significance.

In this chapter, only the simplest problems will be considered and the ideas of simple models will be introduced. The more complicated models will be introduced throughout the book in the chapters dealing with the particular mathematical techniques which are needed for the completion of the solutions.

1.2. REPRESENTATION OF THE PROBLEM

A simple example of the application of these ideas will be given first. The apparatus shown diagrammatically in Fig. 1.1 is to be used for the continuous extraction of benzoic acid from toluene, using water as the extracting solvent. The two streams are fed into a tank A where they are stirred vigorously, and the mixture is then pumped into tank B where it is allowed

to settle into two layers. The upper toluene layer and the lower water layer are removed separately, and the problem is to find what proportion of the benzoic acid has passed into the solvent phase.

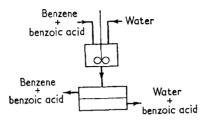


Fig. 1.1. Single-stage mixer settler

The problem is idealized in Fig. 1.2 where the two tanks have been combined into a single stage. The various streams have been labelled and two material balances have already been used, (a) conservation of toluene, and (b) conservation of water. These flow rates have been expressed on a solute

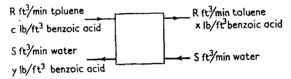


Fig. 1.2. Idealized single-stage solvent extraction

free basis to simplify the analysis. The concentration of benzoic acid in each stream has also been stated and this completes the mathematical model.

So far, it has been assumed that all flow rates are steady, and that toluene and water are immiscible. Further assumptions are now made that the feed concentration c remains constant, and that the mixer is so efficient that the two streams leaving the stage are always in equilibrium with one another. This last fact can be expressed mathematically by

$$y = mx ag{1.1}$$

where m is the distribution coefficient.

The equation is now derived from the model by writing down a mass balance for benzoic acid.

Input of benzoic acid = Rc lb/minOutput of benzoic acid = Rx + Sy lb/min

Since benzoic acid must leave at the same rate as it enters,

$$Rc = Rx + Sy ag{1.2}$$

The pair of equations (1.1) and (1.2) contain four known quantities

(R, S, c, m) and two unknown quantities (x, y), and they can be solved for the unknowns as follows.

$$Rc = Rx + mSx$$

$$\therefore x = \frac{Rc}{R + mS}, \qquad y = \frac{mRc}{R + mS} \tag{1.3}$$

Therefore, the proportion of benzoic acid extracted is

$$\frac{Sy}{Rc} = \frac{mS}{R + mS} \tag{1.4}$$

As a numerical example, if S = 12R, m = 1/8, and c = 0.1; then x = 0.04, y = 0.005, and the proportion of acid extracted is 60%.

At this stage, it can be seen that even in this simple problem, two dimensionless groups which are characteristic of the problem, have arisen quite naturally as a result of the investigation. Putting

$$\alpha = R/mS \tag{1.5}$$

and E = Sy/Rc, equation (1.4) becomes

$$E = 1/(\alpha + 1) \tag{1.6}$$

That is, the proportion extracted is governed solely by the value of the dimensionless group α .

1.3. SOLVENT EXTRACTION IN TWO STAGES

The above example will now be reconsidered, but two stages will be used for the extraction of benzoic acid instead of one stage. Each stage still consists of two tanks, a mixer and a settler, with counter-current flow through the stages. The idealized flow system is shown in Fig. 1.3 where the symbols

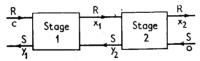


Fig. 1.3. Idealized two-stage extraction

have the same meaning as in the previous example, and the different concentrations in a particular phase are distinguished by suffixes. In accordance with chemical engineering practice, the suffix denotes the number of the stage from which the stream is leaving. The assumptions which were made above are made again, and equation (1.1) is still valid for each stage separately, giving

$$y_1 = mx_1 y_2 = mx_2 (1.7)$$

A benzoic acid mass balance is now taken for each stage.

The fact that benzoic acid must enter and leave a stage at the same rate, gives the two equations

$$Rc + Sy_2 = Rx_1 + Sy_1$$
$$Rx_1 = Rx_2 + Sy_2$$

Using equations (1.7) to eliminate x_1 and y_2 , the inter-stage concentrations,

$$Rc + mSx_2 = (Ry_1/m) + Sy_1$$
 (1.8)

and

$$Ry_1/m = Rx_2 + mSx_2 \tag{1.9}$$

Eliminating y_1 between equations (1.8) and (1.9),

$$R(Rc + mSx_2) = (R + mS)(Rx_2 + mSx_2)$$

$$\therefore R^2c = x_2(R^2 + mRS + m^2S^2)$$

$$\therefore x_2 = \frac{R^2c}{R^2 + mRS + m^2S^2}$$
(1.10)

$$y_1 = \frac{mRc(R+mS)}{R^2 + mRS + m^2S^2}$$
 (1.11)

Again, the proportion of benzoic acid extracted is

$$\frac{Sy_1}{Rc} = \frac{mS(R+mS)}{R^2 + mRS + m^2S^2} \tag{1.12}$$

Introducing the dimensionless groups E and α again from equation (1.5), equation (1.12) becomes

$$E = \frac{\alpha + 1}{\alpha^2 + \alpha + 1} = \frac{\alpha^2 - 1}{\alpha^3 - 1}$$
 (1.13)

Using the same numerical example as before, i.e. S = 12R, m = 1/8, and c = 0.1; then $x_2 = 0.021$, $y_1 = 0.0066$, and the proportion extracted is 79%.

A greater degree of extraction has thus been obtained with two stages than with one stage, everything else being the same.

1.4. SOLVENT EXTRACTION IN N STAGES

This improved extraction leads to the consideration of more than two stages in the extraction system. The algebraic treatment was quite simple for one stage, only requiring the solution of two equations in two unknowns. The application to two stages involved the solution of four equations in four unknowns, and following the same procedure for N stages, it would be necessary to solve 2N equations in 2N unknowns. This is too laborious and would require an individual solution for every integer value of N, and more advanced mathematical techniques are obviously needed to reduce the work. One method using matrix algebra will be illustrated in Chapter 12, but a second method, using finite differences and anticipating the contents of Chapter 9 will be used here.

The general arrangement is as shown in Fig. 1.4 where the flow rates of the two streams are still denoted by R and S, and the benzoic acid concentrations by x and y. The suffix notation is again used to distinguish between

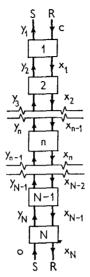


Fig. 1.4. Idealized N-stage extraction

the different states of each stream, the suffix denoting the stage which the stream has just left. This time, a benzoic acid material balance is applied to the general stage n of the system.

Input of acid (lb/min) =
$$Rx_{n-1} + Sy_{n+1}$$

Output of acid (lb/min) = $Rx_n + Sy_n$

Since entry rate and exit rate must be equal,

$$Rx_{n-1} + Sy_{n+1} = Rx_n + Sy_n (1.14)$$

The distribution coefficient equation (1.1) is still valid for any value of n.

$$\therefore y_n = mx_n$$

and equation (1.14) becomes

$$Rx_{n-1} + mSx_{n+1} = (R + mS)x_n$$

Introducing α again from equation (1.5),

$$x_{n-1} + x_{n+1} = (\alpha + 1)x_n$$

or in standard form,

$$x_{n+1} - (\alpha + 1)x_n + x_{n-1} = 0 (1.15)$$

This is a second order linear finite difference equation and the method of solution will be discussed in Chapter 9. The solution is quoted here for

completeness, viz.

$$y_n = mx_n = mc(\alpha^{N+1} - \alpha^n)/(\alpha^{N+1} - 1)$$
 (1.16)

and this may be verified by substitution into equation (1.15). The proportion extracted, E, is given by

$$E = \frac{Sy_1}{Rc} = \frac{\alpha^N - 1}{\alpha^{N+1} - 1}$$
 (1.17)

which gives equation (1.13) for the special case N=2.

TABLE 1.1. Proportion Extracted in N Stages (S = 12R, m = 1/8)

N	1	2	3	5	10
E(%)	60.0	78.9	87.7	95.2	99.4

Table 1.1 gives a few values of E for different values of N for the particular system considered. This shows how the proportion extracted increases with the number of stages, and indicates that more than ten stages are likely to be wasteful whereas one stage gives a poor degree of extraction. This type of problem will be continued in Chapter 13, where the most economical number of stages will be determined by financial considerations.

1.5. SIMPLE WATER STILL WITH PREHEATED FEED

Figure 1.5 illustrates a distillation apparatus consisting of a boiler B with a constant level device C, fed with the condenser cooling water. The steam is condensed in A and collected in the receiver D. Some of the latent heat of

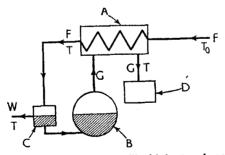


Fig. 1.5. Water still with heat exchanger

evaporation is returned to the boiler by preheating the feed. Denoting the condenser feed rate by F lb/h and the temperature by T_0° F, the exit water temperature by T° F, the excess water over-flow rate by W lb/h and the

distillation rate by G lb/h, the performance of the apparatus can be investigated.

Input of water to the still (lb/h) = FOutput of water from the still (lb/h) = WOutput of steam from the still (lb/h) = G $\therefore F = W + G$ (1.18)

If heat is supplied to the boiler at a rate H Btu/h, the latent heat of evaporation of water is L Btu/lb, and $0^{\circ}F$ is taken as the datum temperature, a heat balance can be taken over the boiler.

Heat input (Btu/h) =
$$H+(F-W)T$$

Heat output (Btu/h) = $212G+LG$
 $\therefore H+GT=(212+L)G$ (1.19)

where equation (1.18) has been used to eliminate W. Equation (1.19) contains two unknown quantities, G and T, and another equation is needed to complete the description. This is obtained from a heat balance over the condenser.

Heat gained by cooling water (Btu/h) =
$$F(T-T_0)$$

Heat lost by condensing steam (Btu/h) = $G(L+212-T)$
 $\therefore F(T-T_0) = G(L+212-T)$ (1.20)

In deriving equation (1.20) it has been assumed that the distillate is cooled to the exit water temperature.

Eliminating G between (1.19) and (1.20),

$$F(T-T_0) = H$$

$$\therefore T = T_0 + H/F$$
(1.21)

From (1.19) and (1.21),

$$H = G(212 + L - T_0 - H/F)$$

$$\therefore G = \frac{FH}{F(212 + L - T_0) - H}$$
(1.22)

This equation gives the rate of distillation in terms of the heat input, and the temperature and flow rate of the cooling water.

If an attempt is made to interpret equation (1.22) for a constant heat supply rate and constant feed temperature, it is seen that as F is decreased, G increases. In fact when $F = H/(212+L-T_0)$ it appears that G is infinite, which is a physical impossibility. Reference to equation (1.21) resolves the difficulty as follows. As F decreases, T increases; but T cannot exceed 212° F as it leaves the condenser, and this gives the restriction

$$T_0 + H/F = T \le 212$$

 $\therefore F \ge H/(212 - T_0)$ (1:23)

If F does not satisfy this inequality, T will remain constant at 212 and equation (1.19) becomes

$$H = LG$$
$$\therefore G = H/L$$

The temperature restriction has a further influence in that the amount of steam produced by the boiler exceeds the capacity of the condenser. Denoting the rate of collection of distillate by D, equation (1.20) becomes

$$F(212 - T_0) = DL$$

$$D = (212 - T_0)F/L$$
(1.24)

The complete solution is thus given by equations (1.22), (1.23), and (1.24); i.e.

$$D = (212 - T_0)F/L$$
 for $F \le H/(212 - T_0)$

and

$$D = \frac{FH}{F(212 + L - T_0) - H} \quad \text{for } F \ge H/(212 - T_0)$$

and this solution is illustrated by the continuous line in Fig. 1.6. This shows that when $F = H/(212-T_0)$, the rate of collection of distillate is a maximum at a value H/L.

The above analysis has been made without reference to heat losses, and an attempt to allow for these would lead to a much more complicated model. A qualitative investigation would suggest that heat losses in the feed line to the boiler would be detrimental, and more serious at low values of F; but heat losses in the vapour line can have two effects. If F is greater than the optimum value, losses from the vapour line will be detrimental, but if F is smaller than the optimum value, heat losses from the vapour line will actually increase the yield. On the basis of these considerations, the second, dotted line has been drawn in Fig. 1.6.

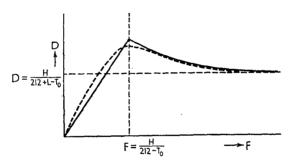


Fig. 1.6. Variation of distillation rate with feed rate

1.6. UNSTEADY STATE OPERATION

In the examples considered so far, the system has been in a steady state, allowing the material entering the system to be equated to the material leaving the system and this has always given algebraic equations. In unsteady state problems, however, time enters as a variable and some properties of the system become functions of time. In the application of conservation laws it is no longer true that the rate of entry of material will equal the rate of exit, since an allowance must be made for material accumulating within the