SOLUTION OF NONLINEAR ALGEBRAIC EQUATIONS

in the Analysis, Design, and Optimization of Continuous Ultrafiltration

GREG FOLEY
Dublin City University • Dublin 9, Ireland

Ultrafiltration for the concentration and purification of macromolecular solutions is an increasingly important unit operation especially in the bioprocessing industries.[1] While it has traditionally formed only a minor part of many chemical engineering undergraduate curricula, the growing importance of bioprocessing within the chemical engineering mainstream means that membranes and their applications are gaining increasing attention. Most unit operations textbooks used in chemical engineering tend to give relatively little coverage of membrane processes in comparison with the more traditional separation techniques such as liquid-liquid extraction, adsorption, and distillation,[2, 3] although there are signs that this is changing somewhat.[4] For now, however, detailed coverage of membrane topics tends be found in specialized books and monographs.[1, 5, 6] While the growing number of textbooks devoted to biochemical or bioprocess engineering has begun to redress this balance somewhat,[7-9] it still has to be said that these textbooks tend to be less mathematical in their focus than traditional unit operations textbooks. The works by Ingham, et al.,[10] and Dunn, et al.,[11] represent a determination to extend mathematical modeling to all aspects of chemical and biochemical engineering but their focus is on dynamic problems where the mathematical problem is almost exclusively one of solving ordinary differential equations. The recent, excellent book by Cutlip and Shacham[12] gives hundreds of interesting and challenging computational problems for the chemical engineering student, presenting a wider range of mathematical challenges, including the solution of non-linear algebraic equations, but there are few problems on bioseparation processes such as ultrafiltration or chromatography. Thus, the chemical engineering undergraduate gets relatively little exposure to sufficiently challenging computational problems in the biologically based downstream processes.

In this paper, we present a variety of problems in the analysis, design, and optimization of the industrially important unit operation of continuous feed and bleed ultrafiltration. The unifying concept in these problems is the solution of non-linear algebraic equations. We solve these using a variety of methods employing easily accessible spreadsheet and graphical tools. The problems described would be suitable for inclusion in a junior- or senior-level unit operations or separations module within a chemical engineering or similar degree program, as long as the students have some prior experience with numerical methods. A problem-based learning approach in which students solve these problems in class using a laptop computer is recommended.

Greg Foley *is a chemical engineer with B.E. and Ph.D. degrees from University College Dublin, Ireland, and an M.S. degree in chemical engineering from Cornell University. He has taught many aspects of chemical engineering to students of biotechnology at Dublin City University for more than 24 years. His main area of expertise and the focus of his research is in membrane processing, especially crossflow microfiltration of microbial cells and the modeling of ultrafiltration and diafiltration processes. He also has an active interest in teaching innovation and has developed numerous initiatives in this area including the use of video podcasting and problem-based learning. He is particularly interested in the interface between teaching and research and the incorporation of research problems into the undergraduate curriculum is one of his ongoing projects.*

CONTINUOUS FEED AND BLEED ULTRAFILTRATION

We consider the example of continuous concentration of a protein solution by the feed and bleed mode illustrated in Figure 1. The protein is assumed to have a rejection coefficient of 1.0, *i.e.*, no protein passes through the membrane. In the feed and bleed configuration, a portion of the product stream (retentate) is recycled back into the feed. This increases the mass transfer coefficient in the module, leading to higher permeate (filtrate) fluxes. Typically, the flowrate through the module greatly exceeds the inlet flowrate, Q_0, and thus the system can reasonably be assumed to be well mixed, *i.e.*, the retentate concentration is taken to be the same as the mean concentration in the module itself.[1] This is in contrast to single-pass operation where there is no recycle and the variation of concentration with distance along the membrane must be accounted for in the analysis.

In all our calculations, we assume that the gel polarization model applies, *i.e.*, we assume that the membrane is operating at the limiting flux, given by[1]

$$J = k \ln \frac{c_g}{c} \tag{1}$$

where k is the mass transfer coefficient (assumed constant), c_g is the limiting or "gel" concentration (constant), and c is the retentate concentration. The gel polarization model is a subset of concentration polarization theory in which the convective flux of solute towards the membrane is balanced by diffusion of solute from the membrane back into the bulk flow.[1] The key result of the concentration polarization analysis is that the flux is related to the solute concentration at the membrane. In general, this concentration is a function of transmembrane pressure, but at high pressures where the flux is constant and equal to its limiting value it can be assumed that the solute concentration at the membrane reaches a limiting value as well. This limiting concentration is denoted c_g.

The solute balance for the system, assuming complete rejection, can be written

$$Q_0 c_0 = Q_1 c_1 \tag{2}$$

where Q_0 is the feed volumetric flowrate, c_0 is the feed concentration, c_1 is the retentate concentration, and Q_1 is the retentate flowrate. An overall balance gives

$$Q_0 = Q_1 + JA \tag{3}$$

where A is the membrane area. Combining Eqs. (1), (2), and (3) and using the perfect mixing assumption gives the following governing equation of a single stage system

$$\frac{Q_0}{kA}\left(1 - x_1\right) - \ln x_1 - \ln \frac{c_g}{c_0} = 0 \tag{4}$$

where $x_1 = c_0/c_1$.

This equation and its extension to multi-stage systems are simple but do not have any analytical solution. Given the range of computational tools readily available to students, however, there is no need to adopt trial-and-error solutions to this equation, even when extended to multi-stage systems, as has been done in the past.[1] Instead, rapid, reliable, and easily implemented numerical methods can be used that will not only give accurate answers to engineering problems but also provide the students with excellent opportunities to practice and apply what they have learned in their numerical method courses.

In the following sections we explore the solution of this equation for a variety of problem types and extend it to multi-stage systems. Numerical examples are provided for each type of problem. Microsoft Excel is used throughout but other packages such as Matlab, Polymath,[12] or Mathematica[13] could just as easily have been used.

PROCESS ANALYSIS

Analysis of a Single Stage System

In this type of problem, it is assumed that the membrane area, the feed flowrate, the feed concentration, and the mass transfer coefficient are known and constant. The goal therefore is to calculate the exit concentration. A numerical example, illustrating semi-manual implementation within Excel of the Newton-Raphson algorithm, is shown in Example 1.

Example 1

We consider a 1L/min feed of a protein solution that enters a single stage continuous feed and bleed ultrafiltration system. The feed enters at 10g/L and c_g can be taken to be 300g/L. The mass transfer coefficient is 3.5×10^{-6} m/s and the area is $2.7 m^2$. Use the Newton-Raphson method to compute the retentate concentration.

Using the numbers provided (and ensuring SI units in all cases), Eq. (4) becomes

$$1.764\left(1 - x_1\right) - 3.401 - \ln x_1 = 0 \tag{Ex. 1.1}$$

The Newton-Raphson algorithm for solution of this equation can be written

$$x_1\left(n+1\right) = x_1\left(n\right) + \frac{1.764\left(1 - x_1\left(n\right)\right) - 3.401 - \ln x_1\left(n\right)}{1.764 + 1/x_1\left(n\right)} \tag{Ex. 1.2}$$

Starting with an initial guess of $x_1 = 0.2$, the method converges (to three decimal places) after the third iteration to give $x_1 = 0.149$ and hence $c_1 = 67$g/L. The algorithm is easily implemented in Excel by inserting $x_1(0)$ in cell A1, the formula for $x_1(1)$ in cell B1, and copying this formula across the first row of the spreadsheet to complete as many iterations as desired.

Analysis of a Multi-stage System—Numerical Solution

The extension of the previous analysis to multi-stage systems is simple and merely involves repeated application of the same basic technique. In a multi-stage system, the retentate from one stage forms the feed to the next. It is easy to show that the governing equation for stage i can be written

$$\frac{Q_0}{kA}\left(x_{i-1} - x_i\right) - \ln\frac{c_g}{c_0} - \ln x_i = 0 \qquad (5)$$

For a system with any arbitrary number of stages, N, the simplest way to solve these equations is to do them sequentially as shown for a three-stage system in Example 2.

Example 2

In this example, 1L/min of a protein solution is fed to a three-stage continuous feed and bleed ultrafiltration system. The feed again enters at 10g/L and c_g can be taken to be 300g/L. The mass transfer coefficient is 3.5 $\times$ 10^{-6} m/s in each stage and the area of each stage is 0.9m^2, thus giving the same total area as Example 1. Use the *Goalseek* tool in Excel to compute the concentration leaving the third stage.

With the numbers supplied, Eq. (5) becomes for the first stage:

$$5.29\left(1 - x_1\right) - 3.401 - \ln x_1 = 0 \qquad \text{(Ex. 2.1)}$$

This equation can now be coded into any cell in Excel and the *Goalseek* tool employed. Putting a guess for x_1 into cell A1, the following formula is coded into Cell B1:

=5.291*(1-A1) – 3.401 – LN(A1)

The Goalseek tool is then accessed *via* the "What If" button in Excel 2007. To solve for x_1, one simply *sets* cell B1 to *value* zero by *changing* cell A1.

Using a guess of $x_1 = 0.2$, gives $x_1 = 0.491$. The equation for the second stage thus becomes

$$5.291\left(0.491 - x_2\right) - 3.401 - \ln x_2 = 0 \qquad \text{(Ex. 2.2)}$$

Solving gives $x_2 = 0.176$ and thus the equation for the third stage becomes

$$5.291\left(0.176 - x_3\right) - 3.401 - \ln x_3 = 0 \qquad \text{(Ex. 2.3)}$$

Solving as before gives $x_3 = 0.061$. Therefore the exit concentration from the final stage is 164g/L, which is considerably greater than the 67g/L achieved with a single stage system of the same total area as found in the previous numerical example.

Analysis of a Multi-Stage System—Graphical Solution

It is clear from Example 2 that the availability of packages such as Excel makes solution of ultrafiltration problems routine and accessible to undergraduate students. The use of a purely numerical approach can leave the student somewhat disconnected from the physics of a problem, however. Graphical techniques have a long history in chemical engineering and while they are somewhat obsolete as purely computational devices, they retain considerable utility as pedagogical tools. In this section, we demonstrate a simple graphical technique for the solution of multi-stage problems that not only allows one to rapidly solve such problems without the aid of a computer, but also helps to explain the operation of the system in a language familiar to chemical engineering students. To start, we let x represent c_0/c where c is the exit concentration from an arbitrary stage. For the first stage our governing equations can thus be written

$$J = k\ln\frac{c_g}{c_0} + k\ln x \qquad (6)$$

$$J = \frac{Q_0}{A}\left(1 - x\right) \qquad (7)$$

Eq. (6) is somewhat analogous to the equilibrium curve typically encountered in equilibrium stage operations such as distillation, liquid-liquid extraction, and absorption. Eq. (7) represents a straight line and can thus be thought of as the operating line of the module. Thus, feed and bleed ultrafiltration can actually be described with much of the same language, and using many of the same methods, as the more conventional unit operations well known to chemical engineers.

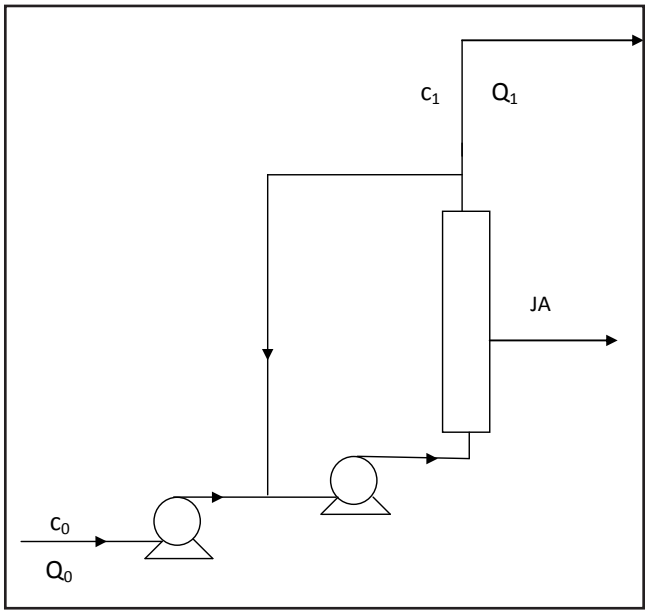

Figure 1. *Continuous feed and bleed ultrafiltration.*

Eq. (7), the operating line, has an x-axis intercept of 1.0 and a y-axis intercept of Q_0/A. The concentration leaving this stage, *i.e.*, x_1, can be found as the point of intersection of the flux curve (analogous to an equilibrium curve), *i.e.*, Eq. (6), and the operating line. The value of this approach is the ease with which it can be extended to multi-stage systems. Carrying out a similar analysis for the second stage, we can write the following expression for the flux in the second stage

$$J = \frac{Q_0}{A}\left(x_1 - x\right) \qquad (8)$$

where we have assumed equal areas. Assuming the mass transfer coefficient is unchanged in the second stage, Eq. (6) can be applied as before. Now, Eq. (8) is a straight line with x-intercept = x_1 and y-intercept = Q_0x_1/A. Clearly, therefore, Eqs. (7) and (8) represent parallel lines and the concentration from the second stage can be evaluated precisely, as done for the first stage. A numerical example for three stages of equal area is shown in Example 3.

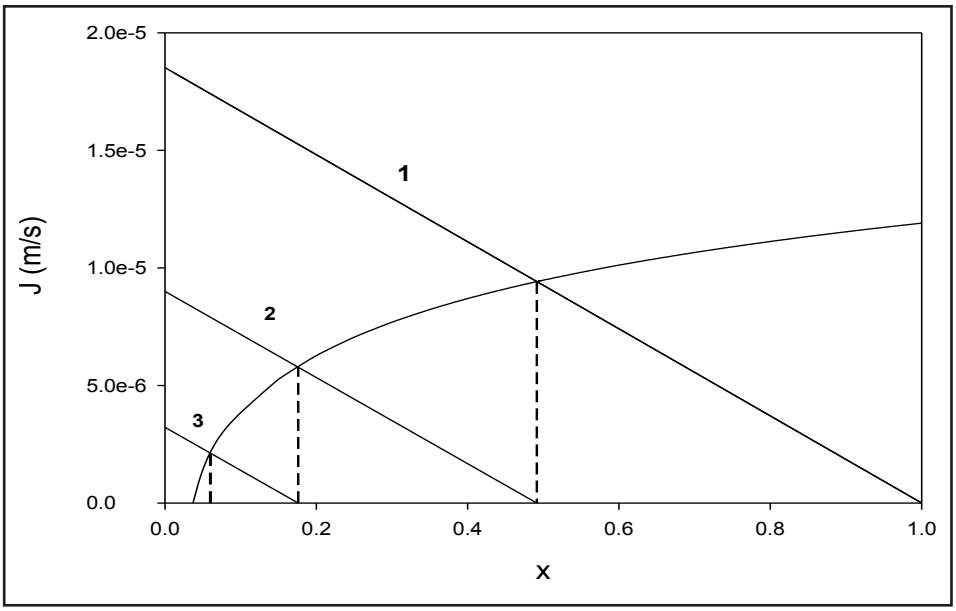

Figure 2. *Graphical construction for multi-stage system.*

Example 3

Here we repeat Example 2 but use the graphical approach described above.

For this problem, Eq. (6) becomes

$$J = 1.19\times10^{-5} + 3.5\times10^{-6}\ln x \qquad \text{(Ex. 3.1)}$$

From Eq. (7) the operating line for the first membrane is

$$J = 1.85\times10^{-5}\left(1 - x\right) \qquad \text{(Ex. 3.2)}$$

Plotting these two expressions leads directly to the construction in Figure 2 and x_3 can be rapidly computed. From the graph we find $c_3 = c_0/0.06 = 167$g/L in close agreement with the numerical solution obtained previously.

DESIGN OF CONTINUOUS UF SYSTEM

In this type of problem, the exit concentration is specified and the mass transfer coefficient is assumed to be known. For a single-stage system, therefore, Eq. (4) becomes

$$A = \frac{Q_0\left(1 - x_1\right)/k}{\ln\left(c_g/c_0\right) + \ln x_1} \qquad (9)$$

In this case, calculation of the required area is trivial. As shown below, however, calculation of the required area for a multistage system is a bit more involved.

Design of a Multi-Stage System With Equal Areas

Using the same notation as in the section entitled "Analysis of a Multi-Stage System—Numerical Solution," we see that the problem now is to solve the N equations described by Eq. (5) but here the unknowns are the x_i for $1 \le i \le$ N-1 and A, the area of each stage. Because the area can be eliminated by rearranging of any one of the equations, however, the system can be reduced to N-1 equations for the intermediate compositions. Nevertheless, unlike the analysis problem described earlier where the equations can be solved sequentially, the design problem requires simultaneous solution of the equations. A numerical example, employing the Solver tool in Excel, is given in Example 4 for a three-stage system.

Optimization of Multi-Stage Systems

In the last section, we showed how the use of a multi-stage system is superior to a single-stage system. There is no reason, however, why the area in each stage should be the same, although in practice using equal areas is probably the most likely choice given the limited range of membrane modules produced by manufacturers. For a system with N stages, the goal, therefore, is to find the values of x_i that minimize the total area, A_t for fixed x_N where

$$A_t = \sum_{i=1}^{N} A_i = \frac{Q_0}{k}\sum_{i=1}^{N}\frac{\left(x_{i-1} - x_i\right)}{\ln\left(c_g/c_0\right) + \ln x_i} \qquad (10)$$

and $x_0 = 1$. The optimum is found by applying the N-1 conditions.

$$\left(\frac{\partial A_t}{\partial x_i}\right)_{x_{j\neq i}} = \frac{\ln\left(c_g/c_0\right)+\ln x_i+\frac{x_{i-1}}{x_i}-1}{\left(\ln\left(c_g/c_0\right)+\ln x_i\right)^2}-\frac{1}{\ln\left(c_g/c_0\right)+\ln x_{i+1}}=0 \text{ for } 1\le i\le N-1 \tag{11}$$

Rearranging in each case gives

$$\ln x_{i+1} = \frac{\left(\ln\left(c_g/c_0\right)+\ln x_i\right)^2}{\ln\left(c_g/c_0\right)+\ln x_i+\frac{x_{i-1}}{x_i}-1}-\ln\frac{c_g}{c_0} \tag{12}$$

In principle, therefore, the values of the x_i that lead to a minimum area are found by simultaneous solution of the N-1 equations represented by Eq. (12). It is worth noting, however, that in the limit where $(1-x_i) \rightarrow 0$, this expression can be simplified somewhat. In that case, we can use appropriate Taylor series expansions ($\ln(x) \approx x - 1$ and $1/x \approx 2 - x$) and neglecting all second order terms, we find

$$x_i = \sqrt{x_{i-1}x_{i+1}} \tag{13}$$

which implies

$$\frac{c_{i+1}}{c_i} = \frac{c_i}{c_{i-1}} \tag{14}$$

which is the relation due to Rautenbach and Albrecht.[4] In Example 5 (next page), we find the exact optimum area for a three-stage system, compare it with the Rautenbach and Albrecht approximation, and with the result obtained previously for a three-stage, equal area system.

Example 4

In this example, 1L/min of a protein solution is fed to a three-stage, equal area, continuous feed and bleed ultrafiltration system. The feed enters at 10g/L and c_g can be taken to be 300g/L. The mass transfer coefficient is 3.5×10^{-6} m/s in each stage and retentate concentration leaving the third stage is 100g/L. The objective is to use the Solver tool to compute the area of each stage.

Applying Eq. (5) and using the relevant numbers (including $x_3 = 0.1$) gives the following equations to be solved

$$\frac{4.762}{A}\left(1-x_1\right)-3.401-\ln x_1=0 \qquad \text{(Ex. 4.1)}$$

$$\frac{4.762}{A}\left(x_1-x_2\right)-3.401-\ln x_2=0 \qquad \text{(Ex. 4.2)}$$

$$\frac{4.762}{A}\left(x_2-0.1\right)-1.098=0 \qquad \text{(Ex. 4.3)}$$

These equations were solved with initial estimates of $x_1 = 0.5$, $x_2 = 0.2$, and $A = 1m^2$. The equations were coded into Excel as shown below in Table 1 and Solver was set the target of *setting* cell B1 to be zero by *changing* cells A1 to A3, subject to the *constraints* B2 = 0 and B3 = 0.

Solver converged successfully giving $A = 0.713m^2$, $x_1 = 0.574$, and $x_2 = 0.264$. Thus, the total area required is $3 \times 0.713 = 2.139m^2$. It would be a useful student exercise to compare the area required if a single stage system had been used. Applying Eq. (9) should give an area of $3.902m^2$, thus showing the advantage of the multi-stage system.

As mentioned above, this system of three equations could have been reduced to two equations by eliminating A from any one of the equations, thus giving two equations that can also be solved with Solver. Again, this would be a useful student exercise.

CONCLUSIONS

Continuous feed and bleed ultrafiltration is a conceptually simple unit operation but the logarithmic dependence of the permeate flux on concentration leads to non-linear algebraic equations, even for the simplest process situations. With modern software and with simple graphical methods, however, these equations can be solved quite easily and there is no reason why they should not be covered as an integral part of an undergraduate module in bioseparation processes. Furthermore, there is plenty of scope here for even more challenging problems using more complex models for the permeate flux.

TABLE 1
Excel Code for Solving System of Algebraic Equations

Column A (Guess)	Column B (Formula)
0.5	=4.762/A3*(1-A1) – 3.401 – ln(A1)
0.2	=4.762/A3*(A1-A2) – 3.401 – ln(A2)
1	=4.762/A3*(A2-0.1) – 1.098

Example 5

Again we have 1 L/min of a protein solution fed to a three-stage continuous feed and bleed ultrafiltration system. The feed enters at 10g/L and c_g can be taken to be 300g/L. The mass transfer coefficient is 3.5×10^{-6} m/s in each stage. The objective is to find the minimum area required to achieve a concentration of 100g/L in the third stage.

The unknowns in this problem are x_1 and x_2 (recall that $x_3 = 0.1$) and Eq. (12) can be written after a little rearranging as

$$\left(3.401+\ln x_2\right)\left(3.401+\ln x_1+\frac{1}{x_1}-1\right)-\left(3.401+\ln x_1\right)^2=0 \quad \text{(Ex. 5.1)}$$

$$1.098\left(3.401+\ln x_2+\frac{x_1}{x_2}-1\right)-\left(3.401+\ln x_2\right)^2=0 \qquad \text{(Ex. 5.2)}$$

Excel Solver was set with the target of satisfying the first equation while the second equation was made a constraint. The initial guesses were $x_1 = 0.5$ and $x_2 = 0.2$. Convergence was achieved giving $x_1 = 0.465$ and $x_2 = 0.209$. Thus, from Eq. (10), the areas of the three stages are $0.967m^2$, $0.664m^2$, and $0.473m^2$, respectively, giving a total area of $2.103m^2$. This compares with $2.139m^2$ in the previous example where equal areas were used. Thus the benefits of using an optimized system rather than using a more convenient equal area system are small indeed.

It is a useful student exercise to compare the exact result found here with the Rautenbach andAlbrecht approximation, Eq. (13). Students should find $x_1 = x_3^{1/3} = 0.464$ and $x_2 = x_3^{2/3} = 0.215$, both of which have values that are very close to the exact answer.

REFERENCES

1. Cheryan, M., *Ultrafiltration and Microfiltration Handbook,* 2nd Ed., CRC Press (1998)
2. McCabe, W., J. Smith, and P. Harriott, *Unit Operations of Chemical Engineering*, 7th Ed., McGraw-Hill (2005)
3. Geankoplis, C.J., *Transport Processes and Separation Process Principles (Includes Unit Operations)*, Prentice Hall (2003)
4. Wankat, P.C., *Separation Process Engineering,* 2nd Ed., Prentice Hall (2007)
5. Rautenbach, R., and R. Albrecht, *Membrane Process*, Wiley-Blackwell (1989)
6. Zeman, L.J., and A.L. Zydney, *Microfiltration and Ultrafiltration*, CRC Press (1986)
7. Belter, P.A., E.L. Cussler, and W.-S. Hu, *Bioseparations: Downstream Processing for Biotechnology,* Academic Press (1988)
8. Harrison, R.G., P.W. Todd, S.R. Rudge, and D. Petrides, *Bioseparations Science and Engineering,* Oxford University Press (2003)
9. Ladisch, M.R., *Bioseparations Engineering: Principles, Practice, and Economics*, Academic Press (2001)
10. Dunn, I.J., E. Heinzle, J. Ingham, and J.E. Prenosil, *Biological Reaction Engineering: Dynamic Modelling Fundamentals with Simulation Examples*, Wiley-VCH (2003)
11. Ingham, J., I.J. Dunn, E. Heinzle, and J.E. Prenosil, *Chemical Engineering Dynamics: Modelling with PC Simulation,* 2nd Ed., Wiley-VCH (2000)
12. Cutlip, B., and M. Shacham, *Problem Solving in Chemical and Biochemical Engineering with POLYMATH, Excel, and MATLAB,* 2nd Ed., Prentice Hall (2007)
13. Foley, H.C., *Introduction to Chemical Engineering Analysis Using Mathematica*, Academic Press (2002) ❐