Appendix B

Numerical Methods

This appendix will discuss a few numerical methods which might be useful to you in solving some of the problems at the end of the chapters.

B.1 Solving Equations

Some equations, such as that of van der Waals, are trivial to solve for some variables (e.g., P or T), but more difficult to solve others (V). As discussed in Chapter 1, the van der Waals equation may be rearranged into a cubic equation for V, and formulas are available to obtain the roots for such equations. Our objective here is to discuss more general methods for obtaining approximate solutions for such equations. One way to approach the solution of the general equation,

$$y = f(x, y) \tag{1}$$

is to rewrite it in the form

$$F(x, y) = y - f(x, y) = 0 \tag{2}$$

With a calculator, it is usually simple to try different values of y, for a given value of x, until the function $F(x, y)$ changes sign and then close in on the root of Eq. (2), until the required accuracy for y is obtained. Such a procedure is known as *trial and error*. Of course, one must be aware that sometimes Eq. (2) may have more than a single real root, as does the van der Waals equation in the two-phase region.

Sometimes, the function $f(x, y)$ can be written in the form

$$y = f(x, y) = g[h(x) + j(x, y)] \tag{3}$$

where h, g, and j are functions. If j is much smaller than h, it may be possible to neglect it completely and solve directly for y. If j is somewhat larger, this first value of y may be used in the right-hand side of Eq. (3) to calculate a corrected value for y. This procedure can be repeated until successive values of y are unchanged to the desired accuracy (convergence). This method is called *successive approximations* and often may be carried out faster than trial and error.

A successive approximation method that does not rely on the y-dependent part of F being small is the *Newton–Raphson* method. As seen in Fig. 1, if a value of y, y_1, gives $F(x, y_1)$, a closer solution to Eq. (2) can usually be obtained by setting

$$y_2 = y_1 - \frac{F(x, y_1)}{(\partial F(x, y)/\partial y)_{x, y=y_1}} \tag{4}$$

Computer programs (such as Mathcad) automatically implement the Newton–Raphson method of finding roots. Usually, such programs require the input of an

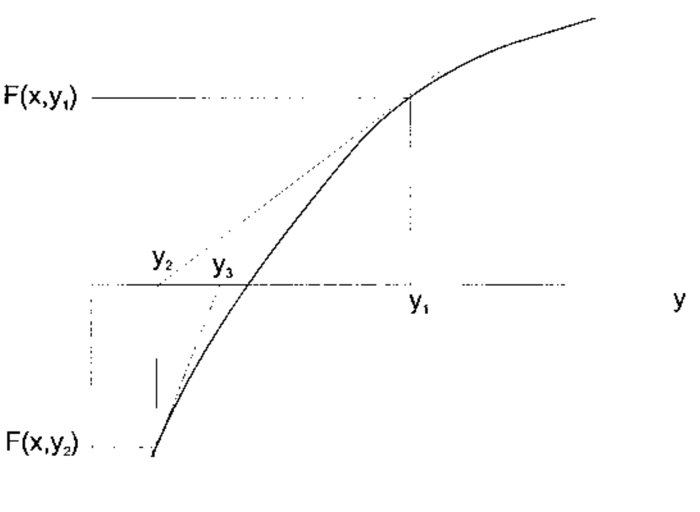

Figure 1

initial guess of the root. However, certain precautions are wise when using such programs. First, it is usually worthwhile to plot or tabulate the function, to see whether it has multiple roots, and to aid in choosing a guess that is sufficiently close to the root of interest, so that it will converge to that root. Second, in cases in which $(\partial F(x, y)/\partial y)_{x,y=y_1}$ is very small, the program may reach the convergence criterion on $F(x, y)$ without identifying the root with sufficient accuracy.

B.2 Fitting Data

We will only discuss the problem of fitting data points to a straight line. In earlier days, this was accomplished by placing a transparent piece of plastic with a straight edge over the data, so as to minimize the sum of the magnitudes of the deviations of the point from the edge.

For data influenced only by small random fluctuations, it can be shown that the proper criterion is a minimization of the sum of the squares of the deviations from the fitting line. Obtaining the best-fitting line by this criterion is known as *linear regression analysis*. Computer programs, such as Mathcad, as well as most scientific calculators can perform linear regression analysis. In case these are not available, the relevant formulas are as follows.

To fit a set of N points (x_i, y_i) to the straight line $y = mx + b$, first calculate D as

$$D \equiv N \sum_i x_i^2 - \left(\sum_i x_i\right)^2 \tag{5}$$

The slope and intercept of the best-fit straight line are then given by

$$m = \frac{N \sum_i (x_i y_i) - (\sum_i x_i)(\sum_i y_i)}{D} \tag{6}$$

$$b = \frac{(\sum_i y_i)(\sum_i x_i^2) - (\sum_i x_i y_i)(\sum_i x_i)}{D} \tag{7}$$

For best accuracy, it is necessary to keep twice as many significant figures in the calculations of the various sums as there are in the original dataset. Books on regression analysis will provide criteria for "goodness of fit" and for the accuracy with which the slope and intercept are known. It is very important to plot the original data points on the same graph as the straight-line fit, to see whether linear regression is appropriate or whether there is a *systematic* deviation of the data from the line. The latter is indicated by the points at the two extremes of the abscissa range tending to be above or below the line. If systematic deviation is observed, a fit to a polynomial function can be employed.

B.3 Numerical Integration

Numerical integration is needed when the functional form of the integrand is such as to preclude analytical integration or when the data to be integrated are obtained in tabular form as the result of measurements. In the latter case, the data have varying amounts of scatter, and linear or polynomial regression should often be use before (analytical) integration.

The simplest method of numerical integration is the trapezoidal method, where the abscissa is divided into intervals and each resulting area is estimated as the abscissa interval times the average of the initial and final ordinate in the interval:

$$\int_{x_0}^{x_{n+1}} f(x)\, dx = \sum_{i=0}^{n} (x_{i+1} - x_i) \frac{f(x_{i+1}) + f(x_i)}{2} \tag{8}$$

A numerical integration of a function using three trapezoids is shown in Fig. 2. The exact integral is the shaded area, and for the function chosen, each of the trapezoids overestimates the area under the curve. The accuracy of the method can, of course, be improved by dividing the range of integration into a larger number of intervals (i.e., using narrower trapezoids). In using the trapezoidal

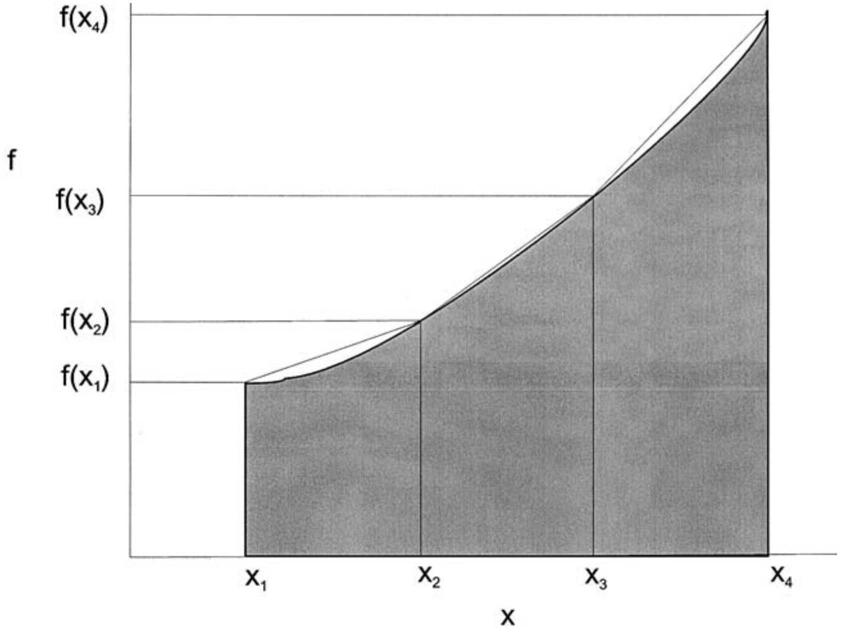

Figure 2 Numerical integration of a function using three variables.

method, the trapezoids do not all have to be of the same width. This is particularly convenient in integrating experimental data, which may not have been obtained at regular intervals of the independent variable.

A more accurate method of numerical integration is by the use of Simpson's rule. This method, however, requires that the integration range be divided into an even number of intervals of equal width h. This requires an odd number of points on the abscissa, which are numbered from 0 to n. Simpson's rule gives

$$\int_{x_0}^{x_n} f(x)\,dx = \frac{h}{3}(f_0 + 4f_1 + 2f_2 + 4f_3 + 2f_4 + \cdots + 4f_{n-1} + f_n) \tag{9}$$

Problems

1. Solve the equation $e^y = xy/(y + xe^{-xy})$ for $x = 5$, finding y with an error of less than 0.001, using both trial and error and successive approximation. Which takes less time?

2. Find the best least-squares straight-line fit to this data:

x	0	0.40	0.70	1.00	1.50	2.00
y	0.87	1.13	1.19	1.42	1.58	1.82

3. Integrate the function $f(x) = e^{-x^2}$, from $x = 1$ to $x = 2$, using the trapezoidal rule with x intervals of 0.25 and using Simpson's rule with the same interval.