assumed in the exact mass calculations. In both modes, during the process of formula generation the user can choose a particular compound and generate species with isotopic nuclei. In this case, the user is prompted for the specification of the particular isotopic atoms to be considered.

Recently a similar program, named MSPI and based almost entirely on heuristics, has been reported in the literature (*21*). The main difference between these programs is that FORMULAS relies not only on heuristic but also on more rigorous graph-theoretical rules. This approach gives our program the possibility of handling additional restrictions, like the degree of unsaturation and the ionization state, in the generation of the possible molecular formulas. This gives the program a more general character which can be appreciated through the fact that the program FORMULAS is able to generate some plausible formulas that are not generated by the program MSPI.

The execution of the program FORMULAS requires an IBM-PC or compatible with 512 Kbytes of RAM and at least one disk drive. Copies of the program, both source and executable files, are available from the authors on a 5.25-in. disk that includes a README executable file with a brief introduction, some notes about notation, and a table of the employed atomic mass values. Send a money order for $15 to any one of the authors.

Determination of Inflection Points from Experimental Data

Daniel E. Stogryn
Mount St. Mary's College
12001 Chalon Rd.
Los Angeles, CA 90049

Plots of experimental data frequently show inflection points, the locations of which are important in an experiment. In chemistry and biochemistry, titrations using pH meters or potentiometric titrations are well-known examples. This communication provides a program for determining the location of an inflection point for those laboratories with access to a computer or workstation with an AT&T UNIX operating system. The program, which is only seven lines long, is written as a UNIX shell procedure and depends on the standard UNIX spline and awk commands. Only five or six data points, not necessarily equally spaced over abscissa values, spanning the inflection point are required for very good results useful at both the research level and in student laboratories.

The spline command provides a set of interpolated points obtained with cubic spline interpolating polynomials (*22*). Each polynomial connects two successive data points in such a way that there is continuity of the first and second derivatives at the point connected by two adjacent polynomials. Spline interpolation has the desirable feature of being less sensitive to "bad" data points than interpolation by a single polynomial spanning the set of data; however, even with the spline interpolation, obviously "bad" points in the neighborhood of the inflection point should be excluded from the analysis. Although the input data need not be equally spaced along the abscissa, the UNIX spline command provides approximately equally spaced interpolated values which can be further processed. The awk command is a pattern scanning and processing language which, in our case, takes the output of the spline command, approximates the point where the second derivative is zero (the inflection point) by locating where the absolute value of a function's increment over approximately equally sized intervals of the abscissa is largest, and then prints the results.

The UNIX shell procedure is shown in Figure 2. To use this shell procedure, a data file with the experimentally obtained coordinates arranged according to either monotone

```
spline -n ${1} < ${2} | awk 'BEGIN {sign = 1}
{inc = previousord - $2; if(NR == 1) {inc = 0; bab = $1;}
if(NR == 2 && inc < 0) sign = -1; sab = $1;
print $1, $2, inc; if (sign*inc >= sign*previousinc)
{inflectpt = $1; previousinc = inc;} previousord = $2}
END {printf("\ninflection point absicssa = %5.2f +- %4.3f\n",\
inflectpt, (bab - sab)/'${1}')}' > ${3}
```

Figure 2. Listing of the UNIX shell procedure for determining the inflection point.

increasing or decreasing abscissa values is prepared. Each line of the data file should have an abscissa value followed by one or more spaces and then the corresponding ordinate value. If a comma is used to separate the abscissa and ordinate values, there should be no space between the comma and the last digit of the abscissa value. In this case, no space is required between the comma and the ordinate value. The shell procedure is invoked as follows:

$ inflectpt number inputfile outputfile

where the $ symbol represents the system prompt, inflectpt is the file containing the shell procedure of Figure 2, inputfile is the name of the data file described above, and outputfile is the name of a file where the output of the shell procedure is stored. Outputfile is optional, so that if it is omitted, the results will be displayed on the CRT rather than stored in the file outputfile. Number is the number of abscissa intervals selected for the spline command's output. It therefore controls the mathematical accuracy of the value of the abscissa at the inflection point assuming the experimental data points are exact. E.g., if the abscissa points in the data file span 1.3 units and number is 20, then the mathematical accuracy would be 1.3/20 = 0.065 units. The output of the shell procedure, in addition to the inflection point and its mathematical accuracy, contains a three-column format with the experimental and interpolated abscissa values in column 1, the corresponding ordinate values in column 2, and the increments in the ordinate value (current value − preceding value) in column 3. In critical situations, where the data near the inflection point is uncertain and the best possible results are necessary, plotting the detailed output can suggest which experimental points are more reliable. If this output is not desired, the removal of "print $1, $2, inc.;" from the fourth line of the shell procedure will give only the inflection point and accuracy.

A potentiometric titration of $HC_2H_3O_2$ with NaOH using a quinhydrone electrode gave the following data (milliliters added NaOH, volts) in a student experiment: (14.70, 0.0910), (15.00, 0.0754), (15.20, 0.0600), (15.40, 0.0171), and (15.60, −0.0162). With number chosen as 50 when the shell procedure is executed, the result is inflection point = 15.33 ± 0.018. The student found the equivalence point to be 15.34 mL of added NaOH from a visual examination of the complete titration curve without being able to give a close estimate of the mathematical accuracy.

LAOCOON PC: NMR Simulation on a Personal Computer

Matthew Clark[2] and Joseph S. Thrasher
University of Alabama
Tuscaloosa, AL 35487

While computer simulation of complex NMR spectra is not new, we have developed a modern version of an NMR

[2] Current address: Tripos Associates, Inc., 1699 South Hanley Road, Suite 303, St. Louis, MO 63144.