

Computer-assisted exercises for physical chemistry

In order to differentiate it from the restricted concept of a programmed instruction scheme, I consider computer-assisted instruction to mean any form of instruction which makes use of a computer to assist the student. In this context, the exercises outlined below have several levels of instructional benefit: (1) As a prerequisite to the use of the computer, the student necessarily must learn to program. Insofar as programming is rapidly becoming an indispensable laboratory technique, the student achieves this goal in a limited but still useful manner. (2) In the past, the introductory physical chemistry course has necessarily over-emphasized ideal systems, in part because the mathematics becomes too cumbersome when real systems are treated. (Note that the mathematics is generally too cumbersome for practical student use, not too difficult inherently.) With the availability of computers, tedious arithmetic is no longer a problem to be evaded. Thus, as the principal instructional aspect of these exercises, students examine the PVT behavior of a real, nonideal, gas—CO₂ in our exercises—and compare various equations of state with the experimental results. In our actual laboratory work one of the first experiments performed is the determination of the isothermal compressibility factor of several real gases, including CO₂, as a function of pressure. By focusing the students' attention on this subject for a few weeks prior to the actual lab, the level of interest and understanding is much greater than usual. (3) As part of the computations, students are introduced to such ideas as series expansions of functions, iterative solutions of equations, and appropriate plotting of data. (4) Finally, by doing computer exercises for the first few weeks of the term, a desirable phase lag is introduced between the lecture and laboratory program. Heretofore, students often "did" an experiment before they had an opportunity to study and discuss the principles; with few exceptions we found this to be unsatisfactory.

A brief outline of the computer-assisted exercises follows below. We have used Dickson's text,¹ supplemented by our computing center's Student Guide. Although there are two remote terminals for the CDC-6400 computer, the waiting time is long and most students use the batch (road-runner) service which permits at most two turn-arounds per day. Thus, if extensive debugging is required, as it may at the beginning, only brief programs should be assigned. In terms of com-

puting time, and thus of funds, the entire series of exercises makes extremely modest demands; we estimate a minute per student as the maximum.

The Exercises

Exercise (1). The Van der Waals equation is expanded in powers of V^{-1} . Then the approximation $V^{-1} = P/RT$ is applied and the series is truncated after the quadratic term leading to

$$Z = PV/RT = 1 + (b - a/RT)(P/RT) + (b/RT)^2 P^2 \quad (1)$$

Students are given the values of the Van der Waals a and b for CO₂ and each is assigned a temperature in the range $320 \leq T \leq 500^\circ\text{K}$ ($1.05 \leq T_R \leq 1.64$). Each student evaluates the compressibility factor at this temperature at 20-atm increments in the range $0 \leq P \leq 300$ atm ($0 \leq P_R \leq 4$). Z is plotted as a function of P .

After the students have been taught the use of the key-punches and have been given the format of the various control cards required to process the job, this exercise goes very smoothly. In the first flush of enthusiasm at getting a printout, the students generally pay little attention to the results. However, some students noted that the monotonically decreasing Z (see the figure) is not the behavior expected and extended the calculation to much higher pressures, observing that Z goes through a minimum at about 1000 atm (depending on temperature, of course). This raises the question of the actual behavior of CO₂. The experimental data² have not yet been introduced and most of the students haven't the expertise or the incentive to search them out. But this is a natural way to bring in corresponding states and reduced equations of state, and the class is soon convinced that the computed minimum in Z at $P \approx 1000$ atm is an artifact—that the trouble lies with eqn. (1) itself—and this leads to a reexamination of the two approximations made in its development. The students quickly convince themselves (either analytically or by including many of the higher terms, a trivial modification of their program that truncation of the infinite series is not the major problem. This focuses attention on the remaining approximation—use of V_{ideal} instead of V_{vdw} . This point is further considered as part of Exercise 2.

Exercise (2). As a continuation of the study of equations of state, the Beattie-Bridgeman equation³ is introduced both as a polynomial in V^{-1}

$$P = \frac{RT}{V} + \frac{\beta}{V^2} + \frac{\gamma}{V^3} + \frac{\delta}{V^4} \quad (2)$$

and as the inverted (truncated) power series in P

$$V = \frac{RT}{P} + \frac{\beta}{RT} + \gamma'P + \delta'P^2 \quad (3)$$

where

$$\gamma' = (1/RT)^2 (\gamma - \beta^2/RT)$$

¹ DICKSON, T. R., "The Computer and Chemistry," W. H. Freeman and Co., San Francisco, 1968.

² "Landolt-Börnstein Tables," Springer-Verlag, New York, 1967, vol. IV, part 4a, p. 297.

³ CASTELLAN, G., "Physical Chemistry," Addison-Wesley Publishing Co., Reading, Mass., 1964, p. 42.

The Beattie-Bridgeman equation is introduced both as a polynomial in V^{-1} and as the inverted (truncated) power series in P . The Van der Waals equation is expanded in powers of V^{-1} . Then the approximation $V^{-1} = P/RT$ is applied and the series is truncated after the quadratic term leading to $Z = PV/RT = 1 + (b - a/RT)(P/RT) + (b/RT)^2 P^2$. Students are given the values of the Van der Waals a and b for CO₂ and each is assigned a temperature in the range $320 \leq T \leq 500^\circ\text{K}$ ($1.05 \leq T_R \leq 1.64$). Each student evaluates the compressibility factor at this temperature at 20-atm increments in the range $0 \leq P \leq 300$ atm ($0 \leq P_R \leq 4$). Z is plotted as a function of P .

This exercise goes very smoothly. In the first flush of enthusiasm at getting a printout, the students generally pay little attention to the results. However, some students noted that the monotonically decreasing Z (see the figure) is not the behavior expected and extended the calculation to much higher pressures, observing that Z goes through a minimum at about 1000 atm (depending on temperature, of course). This raises the question of the actual behavior of CO₂. The experimental data² have not yet been introduced and most of the students haven't the expertise or the incentive to search them out. But this is a natural way to bring in corresponding states and reduced equations of state, and the class is soon convinced that the computed minimum in Z at $P \approx 1000$ atm is an artifact—that the trouble lies with eqn. (1) itself—and this leads to a reexamination of the two approximations made in its development. The students quickly convince themselves (either analytically or by including many of the higher terms, a trivial modification of their program that truncation of the infinite series is not the major problem. This focuses attention on the remaining approximation—use of V_{ideal} instead of V_{vdw} . This point is further considered as part of Exercise 2.

Exercise (2). As a continuation of the study of equations of state, the Beattie-Bridgeman equation³ is introduced both as a polynomial in V^{-1}

and as the inverted (truncated) power series in P

where

$\gamma' = (1/RT)^2 (\gamma - \beta^2/RT)$