

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.

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$$\begin{aligned} \delta' &= (1/RT)^3 [\delta - 3\beta\gamma/RT + 2\beta^2/(RT)^2] \\ \beta &= RTB_0 - A_0 - Rc/T^2 \\ \gamma &= -RTB_0b + A_0a - RB_0c/T^2 \\ \delta &= RB_0bc/T^2 \end{aligned}$$

The Beattie-Bridgeman constants A_0 , a , B_0 , b , and c for CO_2 are provided and each student computes the compressibility factor at 20-atm increments to 300 atm at the same temperature as previously, using eqn. (3). This exercise is primarily for the purpose of programming experience; the relatively complicated expressions lead to syntactical errors in parenthetical expressions, but otherwise the program is straightforward.

Part B. The Van der Waals equation is solved for the molar volume at 100 atm by iterative methods. Because of its simplicity, the first of the methods described by Dickson⁴ is used: The Van der Waals equation is written in the form $V = F(V)$; an estimate of V is substituted into $F(V)$, leading to an improved value for V . This, in turn, is substituted into $F(V)$, leading to a still better approximation, etc.

This exercise introduces more programming ideas and also the whole problem of convergence as well as the meaning of a solution to an equation from a mathematical and physical point of view.

Although not discussed in detail, the compressibility factor computed from eqn. (3) is exact to $O(P^3)$ and the results differ greatly from the approximate Van der Waals computation of exercise (1). Z_{\min} now occurs at about the correct pressure, and $Z > 1$ at 300 atm.⁵ Also, the temperature dependence of Z (obtained by intercomparison of various isotherms) is much more like that predicted by corresponding states. The agreement with experimental data is poorest near $T_R = 1$, of course, (see the figure) and this provides an opportunity to discuss the relative effectiveness of temperature (kinetic energy) and intermolecular forces. At $T_R = 1.03$ the experimental density of CO_2 at 200 atm is 0.84 g/cm^3 and the distinction—or lack of it—between liquids and dense gases, and the continuity of states, is forcibly driven home when students actually compute similar values, as they do in solving the Van der Waals equation exactly. Near $T_R = 1$, $V_{\text{vdw}} \approx 0.5 V_{\text{ideal}}$ at high pressures and it becomes obvious why eqn. (1) is such a poor approximation under these conditions.

Exercise (3). The study of equations of state is concluded with an examination of the Dieterici equation. The critical constants of CO_2 are listed but not the Dieterici a and b . In analogy with the Van der Waals case, the Dieterici equation is expanded in powers of V^{-1} and truncated at the quadratic term, the substitution $V^{-1} = P/RT$ is made, and the resulting equation

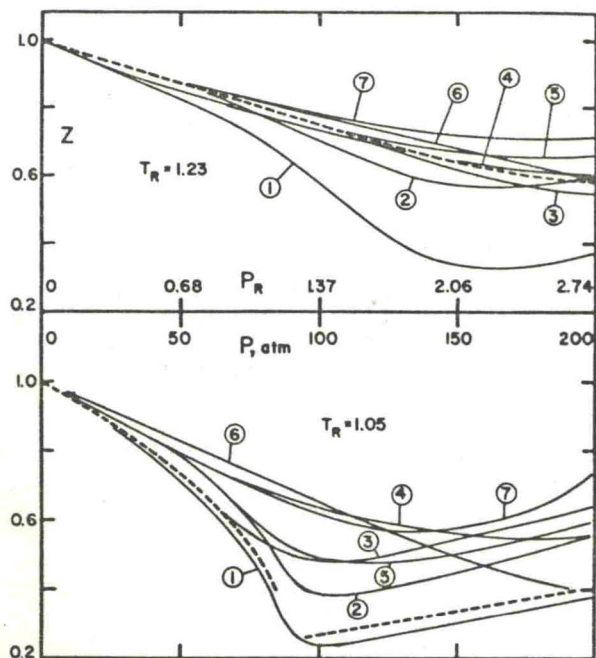
$$Z(\text{approx}) = 1 + (1/RT) (b - a/RT)P + (1/RT)^2 [0.5(a/RT)^2 + b^2 - b(a/RT)] P^2 \quad (4)$$

is used to evaluate an approximate compressibility factor at 20-atm increments, as before. Now that it is obvious to the students that the approximations used in developing eqn. (4) are quite poor, the Dieterici equation is solved exactly for volume at each pressure by the Newton-Raphson iteration procedure⁶ and this value is used in the exact equation

$$Z(\text{exact}) = 1 + (V/(V - b)) \exp(-a/RTV) \quad (5)$$

This is repeated at 20-atm increments, as before. The values P , V_{ideal} , $V_{\text{Dieterici}}$, $Z(\text{approx})$, and $Z(\text{exact})$ are tabulated and graphed.

This program is quite elaborate and students have some difficulty in getting the whole program to run. Subroutines, which would help to keep the logic straight, have not been introduced. The iteration is not completely straightforward since the function has singularities and in some instances the iteration would not converge. Again, the distinction between a physically



Compressibility factor, Z , as a function of pressure for CO_2 . Top: $T = 373^\circ\text{K}$; $T_R = 1.23$. Heavy dashed line is experimental behavior from "Landolt-Bornstein Tables" (see footnote 2). Curve 1 is the Dieterici equation according to eqn. (4) of the text with $a = 4.620 \text{ atm}^2 \text{ mole}^{-2}$, $b = 0.0463 \text{ l mole}^{-1}$; Curve 2 is computed for the Van der Waals equation without approximation using $a = 3.610 \text{ atm}^2 \text{ mole}^{-2}$, $b = 0.0429 \text{ l mole}^{-1}$; Curve 3 is calculated from a fourth-order virial equation using the virial coefficients determined by E. G. Butcher and R. S. Dudson, *Proc. Roy. Soc. (London)*, 277A, 448 (1964); Curve 4 is the virial form of the Dieterici equation according to eqn. (4) of the text; Curve 5 is the Beattie-Bridgeman equation, according to eqn. (2) of the text; Curve 6 is the virial form of the Van der Waals equation as expressed in eqn. (1) of the text; Curve 7 is the virial form of the Beattie-Bridgeman equation according to eqn. (3) of the text. Bottom: Curves keyed as above. Experimental data for $T_R = 1.03$; insufficient data to permit reliable interpolation near the minimum; Curve 3 computed with virial coefficients evaluated at $T_R = 1.02$.

meaningful solution, i.e., $V > b$, and a purely mathematical solution is emphasized.

By now the students have become so used to inputting data to the computer they are at first confounded when the values of a and b are not supplied. (They are to be evaluated from the critical constants, a supplemental problem which also emphasizes that the computer does not supplant analysis.) Some looked for values in the literature⁷ and were even more puzzled to find that the quoted values depend on temperature: we capitalize on this to discuss temperature-dependent virial coefficients and suggested that the Beattie-Bridgeman equation be reexamined from this point of view.

Student response to this aspect of the laboratory program has been enthusiastic even though many students admitted to spending ten or more hours on debugging some of their programs. The amount of material to which the students are exposed is so great that

⁴ Dickson, p. 113 (see footnote 1).

⁵ Actually, the approximate, truncated, Beattie-Bridgeman equation, eqn. (3), overcompensates compared to the Van der Waals equation. An exact solution (from eqn. (2)) indicates that $Z < 1$ for all temperatures and pressures in our range (see figure).

⁶ Dickson, p. 114 (see footnote 1).

⁷ Partington, J. R., "An Advanced Treatise on Physical Chemistry," John Wiley & Sons, Inc., New York, 1949, Vol. I, p. 684, 711.

it is unreasonable to expect that they can assimilate more than a small part of it, but they definitely do understand the distinction between real and ideal gases.

I found the preparation of the exercises very stimulating since I, like all students of my generation, never had the opportunity to examine equations of state of real

gases very carefully. The type of information that now becomes readily available is illustrated in the figure; with the programs available, extension to other gases is a trivial matter.

Readers who would like copies of the three exercises are invited to write for them.

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Computer Demonstrated Lenz-Ising Model

The Lenz-Ising Model has found wide use in the study of co-operative phenomena.² Gas-liquid and liquid-liquid critical phenomena, magnetic-curie points, and helix coil transitions are examples of the diversity of problems to which the model has been applied. Although the model is conceptually simple, its wonders are embedded deep within the mathematics used in its solution. The phenomena associated with the model in two dimensions (most spectacularly a critical temperature) are given *Deus ex machina* in most treatises on statistical mechanics leaving the student at an uncomfortable level of abstraction. This article describes a simple computer approximation to the Lenz-Ising model which demonstrates the predicted properties in the concrete terms of a computer printout of the ordering of an initially random Lenz-Ising lattice.

The heart of the program is two lattices, the Lenz-Ising lattice A, the elements of which can have the value ± 1 , and a second similar lattice B, used to store information. The lattice size and number of dimensions can be varied as can the energy e needed to change the sign of an element as well as the temperature of the system.

Initially, lattice A is populated with random ± 1 (-1 raised to a random integer power between 0 and 9). The individual elements of ± 1 have two forces acting on them; random "thermal" force, and the force of the nearest neighbor interaction trying to make the sign of all the nearest neighbors the same.

The nearest neighbor force is determined for each element $a(i,j)$ of A with the help of an index $Q(i,j)$, the sum of all the nearest neighbor lattice elements; thus in two dimensions

$$Q(i,j) = a(i-1,j) + a(i+1,j) + \dots + a(i,j+1)$$

If $Q(i,j)$ is less than 0, the majority of nearest neighbors are -1 and the element of lattice B, $b(i,j)$ is set equal to -1 . If $Q(i,j)$ is greater than 0, $b(i,j)$ is set equal to $+1$; and if $Q(i,j) = 0$, $b(i,j) = a(i,j)$.

Having decided what the sign of an element would be from just nearest neighbor interaction, the program considers random thermal forces. To change the sign of an element the thermal energy kT must overcome the en-

ergy of transition E arising from an energy barrier e as well as the force of its nearest neighbors. The energy of nearest neighbor interaction will be proportional to the absolute value of Q . The factor $\exp[-(e + |Q|/kT)]$ will give a number between 0 and 1 proportional to the probability that an element will have enough thermal energy to change sign. In order to determine whether this element is one of the lucky ones having enough energy, a random number between 0 and 1 is generated. If the random number is smaller than $\exp[-(e + |Q|/kT)]$, element $b(i,j)$ is changed to $-b(i,j)$.

After going through all of the elements of A and storing the information in B, the program sets lattice A equal to B and the process of determining which elements will change sign is begun over again.

In two dimensions, below the critical temperature, nearest neighbor forces succeed in ordering the lattice, while above the critical temperature no ordering occurs. The dynamics of the model, mimicking real critical phenomena, become very sluggish near the critical temperature. In fact, because of the great number of steps needed to order the system just below the critical temperature, this temperature is determined to better than one significant figure only with great patience.

Interestingly enough with $T = 0$ and therefore only nearest neighbor forces active, the lattice is seldom able to order itself. As soon as four or more adjacent elements form a rectangle they become impregnable to only nearest neighbor forces. At most an element of this configuration can have only two neighbors of different sign, and thus it cannot be forced to change its sign. It would seem that the random thermal forces are necessary to break up these otherwise unassailable domains.

The computer model was not intended to be rigorous; several better approximations to the Lenz-Ising lattice are evident. I think, however, that these improvements would be needless complications adding nothing to the pedagogic value of the program. The original computer program (in Basic) is available from the author on request.

¹ Work performed at Dartmouth College.

² BRUSH, S. G., *Rev. Mod. Phys.*, **39**, 883 (1967).

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