

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

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

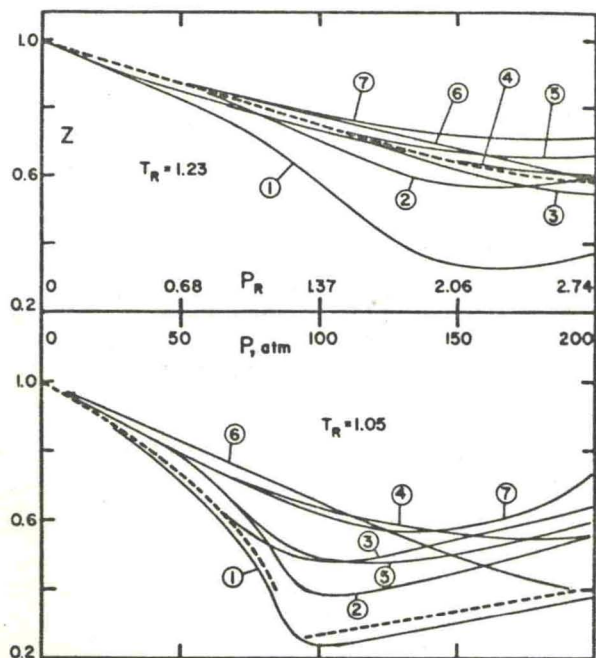
$$Z(\text{approx}) = 1 + (1/RT) (b - a/RT)P + (1/RT)^2 [0.5(a/RT)^2 + b^2 - b(a/RT)] P^2 \quad (4)$$

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.