

Comparisons of Equations of State in Effectively Describing PVT Relations

It is difficult to find quantitative information, especially in a textbook, that shows how well an equation of state will describe the PVT relations of any given gas. Generally the student's only information on the subject has come from one or two comparative calculations. This small sampling of the data can, of course, lead to some bad misconceptions. For example, the molar volume of CO₂ gas at 70 atm and 31°C calculated from the van der Waals equation is very close to the experimental value. The calculated volume, however, at only 5 atm higher and the same temperature is in error by more than 40%. Since the above change takes one through the critical point, one might expect some rather unusual behavior in this region. However, many large deviations may be found under circumstances which are more difficult to predict. For example, for methane gas at 0°C (considerably above the critical temperature) the van der Waals equation predicts a value for the molar volume which is 7.5% high at 100 atm pressure, within 1% at 165 atm and 17% low at 400 atm. Under the same conditions, the Dieterici equation predicts very low values at moderate pressures (38% low at 150 atm) but agrees well with the experimental data at higher pressures (less than 5% low at 600 atm).

The reason for the lack of comprehensive information in the literature about the performance of an equation of state is understandable. The degree of success of an equation in describing PVT relationships depends not only on the temperature and pressure, but on the physical and chemical properties of the gas. Hence, at first, it appears that a large body of information is necessary for an evaluation to be made. Fortunately, as implied in the Law of Corresponding States, all

gases—to a fairly good approximation—show similar PVT relations when compared in the same reduced state. This generalization greatly simplifies the problem of presenting the evaluation information. The extent to which the Law of Corresponding States is valid can be seen from the graph in Figure 1, originally presented by Goug-Jen Su.¹ The compressibility factor $z = PV/RT$ is plotted versus the reduced pressure ($\pi = P/P_c$) for several values of the reduced temperatures ($\tau = T/T_c$). P_c and T_c are the critical state pressure and temperature, respectively. From this graph, it is evident that, to a good approximation, all gases follow the same reduced isotherm when z is plotted versus the reduced pressure. This behavior provides a convenient method for comparing the predictions of an equation of state with the experimental

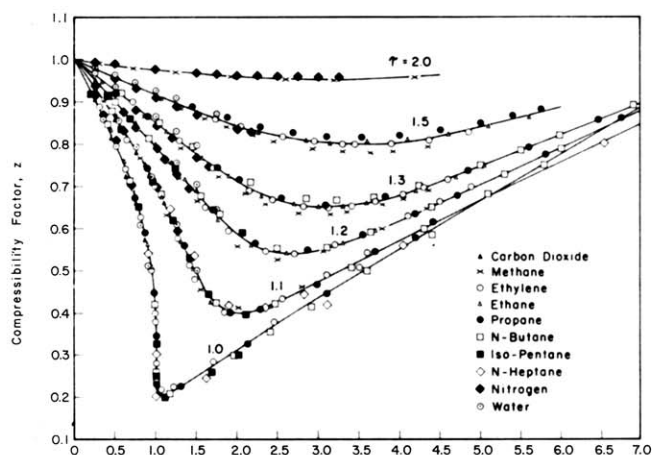


Figure 1. Graph of the compressibility factor for a number of gases versus their reduced pressure at several reduced temperatures. The data taken from Goug-Jen Su (see footnote 1) illustrate the validity of the principle of corresponding states.

¹ Goug-Jen Su, *Ind. Eng. Chem.*, **38**, 803 (1946).

Equations of State (1 Mole) Examined in this Study

	Equation of state	Equation of state (reduced form)	Compressibility factor (reduced form)
van der Waals	$P = \frac{RT}{V-b} - \frac{a}{V^2}$	$\pi = \frac{8\tau}{3\varphi-1} - \frac{3}{\varphi^2}$	$z = \frac{3}{8} \left(\frac{\pi\varphi}{\tau} \right)$
Berthelot	$P = \frac{RT}{V-b} - \frac{a}{TV^2}$	$\pi = \frac{8\tau}{3\varphi-1} - \frac{3}{\tau\varphi^2}$	$z = \frac{3}{8} \left(\frac{\pi\varphi}{\tau} \right)$
Modified Berthelot	$P = \frac{RT}{V} \left[1 + \frac{9PT_c}{128P_cT} \left(1 - \frac{6T_c^2}{T^2} \right) \right]$	$\varphi = R' \left[\frac{\tau}{\pi} + \frac{9}{128} \left(1 - \frac{6}{\tau^2} \right) \right]$ where $R' = RT_c/P_cV_c$	$z = \pi\varphi/R'\tau$ or $z = 1 + \frac{9}{128} \frac{\pi}{\tau} \left(1 - \frac{6}{\tau^2} \right)$
Dieterici	$P = \frac{RTe^{-a/VRT}}{V-b}$	$\pi = \frac{\tau e^{(2-2/\tau\varphi)}}{2\varphi-1}$	$z = 2\pi\varphi/\tau e^2$

a and b are constants different for each equation of state.

behavior of a gas. The equations of state we will be considering can be written in a reduced form; that is, an equation relating τ , π , and the reduced volume, $\varphi = V/V_c$. When written in the reduced form, the equations become completely general. All constants identifying a particular gas (such as the van der Waals a and b) cancel out. A graph of z calculated from the reduced equation as a function of π at various τ values then applies to any gas. We will consider the solid line in Figure 1 to be a good representation of the experimental PVT properties of any gas. A comparison of this curve with the one obtained from the reduced equation of state will show how well the calculation represents the data.

We have chosen to consider the four commonly encountered, two-parameter equations of state listed in the table. With the aid of a Hewlett-Packard calculator (x - y plotter system), we have plotted z versus π at various reduced temperatures for each of the four equations. The smoothed experimental data from Figure 1 are included for comparison. Figures 2-5 cover the reduced pressure range $\pi = 0$ -5. Since critical pressures of most substances vary from 50 to 100 atm, the pressures considered in these graphs generally extend from 0 up to 250-500 atm, a range in which an equation of state might be expected to have utility. The graphs allow one to see at a glance the extent to which the equation of state describes the PVT relations of the real gas under a given set of τ and π conditions. A few general observations that can be made are

1) The rather striking limitations of all four equations are evident. It is interesting that at $\tau = 2$, for example, the van der Waals equation predicts no better z values than the ideal gas equation ($z = 1$), the z values from the van der Waals equation being about as much below as those of the ideal gas are above the experimental value.

2) In some regions of the graph, however, the fit of the experimental data becomes very good; for example, the van der Waals equation at $\pi < 1$ for τ values in the range 1.0-1.2, the Berthelot and the Dieterici equation for $\pi < 1$ at $\tau = 1$, and the modified Berthelot equation for π values up to 3 at $\tau = 2$.

3) The modified Berthelot equation, being linear in pressure, begins to deviate widely from the experimental data at $\pi > 3$.

4) In general, the van der Waals equation is superior to the other three in predicting compressibility factors, but its success varies widely with T and P conditions as already noted.

Important applications of equations of state have to do with corrections of experimental thermodynamic data to standard state conditions. Since these calculations involve relatively low pressures, it is instructive to expand the $\pi < 0.6$ regions of Figures 2-5. This is done in Figures 6-9. A few general observations are

1) The performance of all the equations is, of course, much better in this low reduced pressure region. In some regions, the fit of the experimental data is excellent; for example, the van der Waals equation at $\pi = 1.2$.

2) The Berthelot and Dieterici equation are very inadequate for quantitative calculations.

3) The Modified Berthelot equation, which was designed specifically for the low pressure region, gives z values that are consistently high.

Since the predictions of compressibility factors by the Modified Berthelot equation all differ in the same direction, it seems reasonable to modify the semi-em-

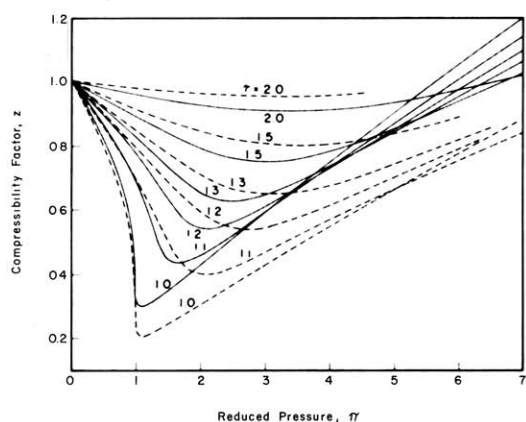


Figure 2. Comparison of the experimental z (dotted lines) with the z values calculated from the van der Waals equation of state (solid lines).

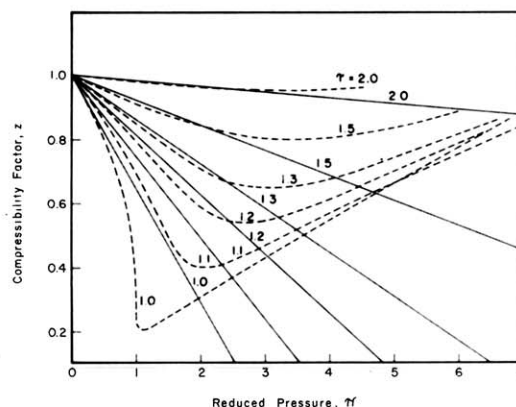


Figure 4. Comparison of the experimental z values (dotted lines) with the z values calculated from the Modified Berthelot equation of state (solid lines).

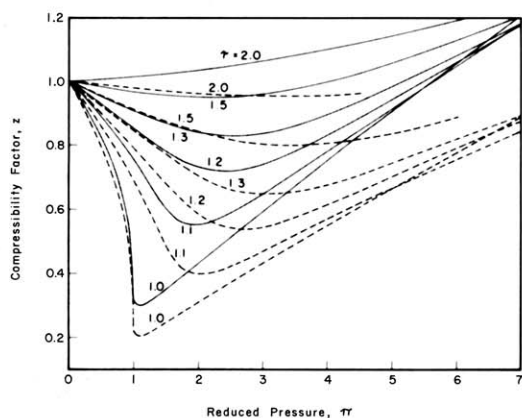


Figure 3. Comparison of the experimental z values (dotted lines) with the z values calculated from the Berthelot equation of state (solid lines).

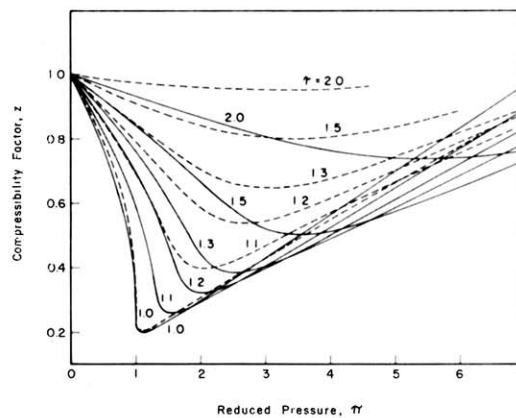


Figure 5. Comparison of the experimental z values (dotted lines) with the z values calculated from the Dieterici equation of state (solid lines).

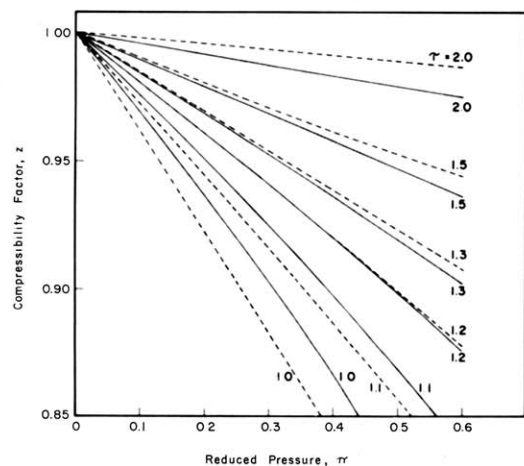


Figure 6. Comparison of the experimental z values (dotted lines) in the low pressure region with the z values calculated from the van der Waals equation of state (solid lines).

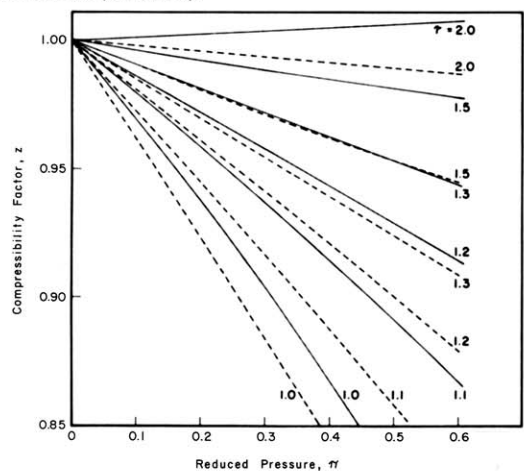


Figure 7. Comparison of the experimental z values (dotted lines) in the low pressure region with the z values calculated from the Berthelot equation of state (solid lines).

pirical constants of this equation to improve the agreement with the experimental data. This we have done by obtaining a least squares fit of the experimental data (in the form of the Modified Berthelot equation) for values of π from 0 to 0.6, and for the six τ values of 1.0, 1.1, 1.2, 1.3, 1.5, and 2.0. The result is

$$PV = RT \left[1 + \frac{PT_c}{17P_cT} \left(1 - \frac{15T_c^2}{2T^2} \right) \right] \quad (1)$$

A comparison of this equation with the experimental data is shown in Figure 10. The new constants are seen to produce a better over-all fit of the experimental data, and at the same time make for a less cluttered equation. We have used the Modified Berthelot equation with the new constants in fugacity coefficient calculations, standard state entropy corrections, and with calculations of the effect of pressure on heat capacity (requires a $\partial^2 P / \partial T^2$ derivative) with slightly better results than are obtained with the old set of constants.

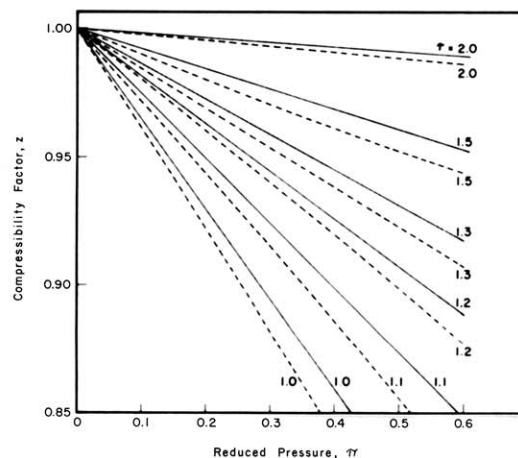


Figure 8. Comparison of the experimental z values (dotted lines) in the low pressure region with the z values calculated from the Modified Berthelot equation of state (solid lines).

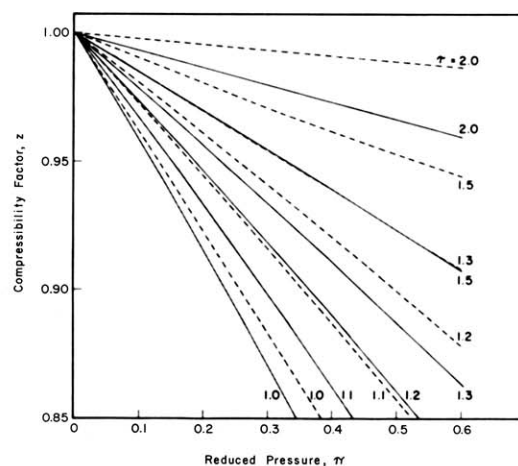


Figure 9. Comparison of the experimental z values (dotted lines) in the low pressure region with the z values calculated from the Dieterici equation of state (solid lines).

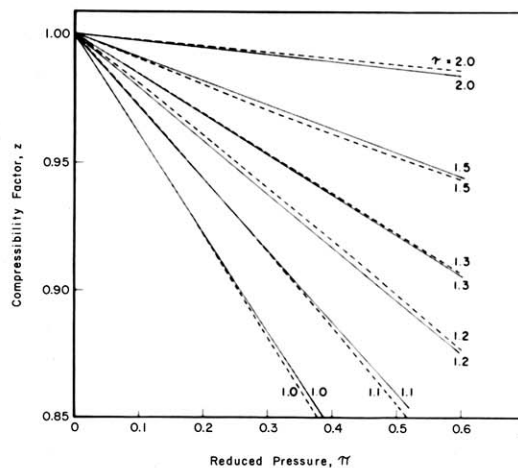


Figure 10. Comparison of the experimental z values (dotted lines) in the low pressure region with the z values calculated from eqn. (1) (solid lines).

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