

The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and that elucidate difficult concepts. Manuscripts should not exceed ten double-spaced pages if possible and should be accompanied by the originals of any figures or photographs. Please submit them to Professor James O. Wilkes (e-mail: wilkes@umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

# CHOOSING AND EVALUATING EQUATIONS OF STATE FOR THERMOPHYSICAL PROPERTIES

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Two kinds of pressure-volume-temperature P- $\nu$ -T diagrams for real substances are usually introduced in the first undergraduate thermodynamics course (hereafter, "thermo I"): a typical P- $\nu$ -T diagram for a substance that contracts on freezing, *e.g.*, carbon dioxide, and a P- $\nu$ -T diagram for a substance that expands on freezing, usually water (see, for example, References 1-4). The relevance of the P- $\nu$ -T data is usually discussed, and different P- $\nu$ -T functions or equations of state are introduced. From this moment until the end of their professional life, chemical engineering students (or chemical engineers) will have to deal with the P- $\nu$ -T relations, in one way or another.

Most chemical engineers will never develop a new EOS, but they will often be in the position of having to select an equation that is the most appropriate for a specific situation. De Nevers and Seader<sup>[5]</sup> pointed out ten years ago that students must learn that "computer answers may depend strongly on which correlations for thermodynamic properties are used. Students need to learn of the many sources of such correlations, along with their limitations and recommended regions of applicability. Also, they need to be aware of experimental sources of data and how to make comparisons between experimental data and empirical correlations."

It is well known that practical engineering applications are deeply affected by fundamentals of thermodynamics. Harvey

and Laesecke<sup>[6]</sup> recently stated, "Engineers should learn the value of thermophysical properties in college." We agree with this statement. Students must be able to choose from among several methods and be aware of how their choice may depend on the nature of the system and state conditions; moreover, they should be exposed to this matter at an early stage of their career.

In traditional chemical engineering curricula, students start to evaluate different models using process simulators such as ASPEN PLUS, ProSim, or ChemStation in their chemical process courses, typically during the third and/or fourth year

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of their studies. In this work, we give an example of how students can be introduced to this topic from an early stage in their career (thermo I), continuing progressively to their professional life (or graduate studies). We present a thermo project where the student will need to use the Internet, handle some software, and read tables.

## PROJECT STATEMENT

Carbon dioxide ( $\text{CO}_2$ ) has been studied since the days of van der Waals, since it exhibits supercritical behavior at moderate conditions. Nowadays,  $\text{CO}_2$  is used in a variety of fields, *e.g.*, in the oil industry (as a carrier gas for enhanced oil recovery) and in “green chemistry,” where research efforts are under way to identify sustainable processes and products using  $\text{CO}_2$ -related technology. Carbon dioxide is extremely attractive in industrial applications because it is the second most abundant and the second least expensive solvent on earth.

In this project, the student is asked to evaluate the P- $\nu$ -T prediction capabilities of different models for carbon dioxide. They are asked to obtain P $\nu$  (or P $\rho$ , where  $\rho = 1/\nu =$  density) diagrams for carbon dioxide showing at least three isotherms, 278.15 K, 198.15 K, and 360 K, for a pressure range from 0.51795 MPa up to 100 MPa, in the gas and liquid phases, as well as the vapor-liquid equilibrium region (from the triple point [ $T_t = 216.592$  K,  $P_t = 0.51795$  MPa] up to the critical point). They are told to compare the volume (or density) predictions in each phase (including the critical region) obtained from

- Two cubic equations of state (*e.g.*, Soave-Redlich-Kwong<sup>[7,1]</sup> and Peng-Robinson<sup>[8,1]</sup>)
- A three-parameter corresponding states method (*e.g.*, Lee-Kesler<sup>[9,1]</sup> tables)
- A multiparametric EOS for  $\text{CO}_2$  (*e.g.*, Span-Wagner<sup>[10,11]</sup>)
- Tables of thermodynamic properties for  $\text{CO}_2$  (IUPAC<sup>[12]</sup> tables)

For extra credit, the student can comment on the use of the virial EOS (truncated at the second virial term, in the density expansion) and the Rackett<sup>[13,14,1]</sup> equation for the determination of volume for the gas and saturated liquid phases, respectively.

The tables mentioned in Section d, below, are from fits of thermodynamic properties to multiparametric equations, *i.e.*, they are smoothed data. But these tables<sup>[12]</sup> are based on older carbon dioxide data. We believe that the Span-Wagner equation<sup>[10]</sup> is the best representation of the experimental data for carbon dioxide and should be used as the standard against which to test the other equations of state and the corresponding states method.<sup>[15]</sup> Span and Wagner made a careful analysis of all the experimental data for carbon dioxide, including recent data, and excluded data that did not satisfy the thermodynamic consistency conditions when fitting their equation of state.

## Justification

- a. This project would not have been feasible for a thermo I course ten to fifteen years ago, but with the availability of computers, software, and the Internet, it is now rather straightforward. Textbooks come with computer-aided strategies for solving cubic equations of state, such as a) the use of “meta-computing” software involving the use of packages such as Maple, Mathematica, Mathcad, and Matlab<sup>[*i.e.*,1,3]</sup>; b) the use of spreadsheets such as EXCEL,<sup>[*i.e.*,3]</sup> or c) the supply of a “code” that can be used for a specific cubic or multiparametric equation of state.<sup>[2,3]</sup> Additionally, several sites can be found on the Internet where on-line cubic EOS software is available at no charge.<sup>[*i.e.*,16]</sup>
- b. Corresponding-state correlations are usually introduced in textbooks<sup>[1-4]</sup> in graphical or tabular form. We believe that students must become familiar with the use of tables and graphs, but we should also keep in mind the pedagogic importance of the implementation of corresponding-state principles by meta-computing software, as was recently discussed by Smith, *et al.*<sup>[17]</sup>
- c. Students should also be exposed to state-of-the-art multiparametric EOS available in up-to-date databases. This can be pursued through the Internet, where leading institutions such as NIST or DECHEMA have friendly web pages. For example, the NIST chemistry webbook<sup>[11]</sup> contains thermophysical properties for 33 pure substances. Tester and Modell<sup>[18]</sup> list in Chapter 13 of their book some of the commonly used sources of pure component and mixture data in both published and electronic form. Additionally, they give examples of United States research centers that focus on physical property measurements and data correlation. Ideally, recent developments in molecular-based EOS should also be included. Unfortunately, to the best of our knowledge, molecular-based EOS (*e.g.*, Statistical Associating Fluid Theory, or SAFT<sup>[19]</sup>) software is not yet available for use at the undergraduate level. The availability of such software in the near future is likely, however, as these kinds of EOS are already included in graduate-level textbooks<sup>[18,20]</sup> and in at least one introductory textbook.<sup>[3]</sup>
- d. Students should become familiar with the use of tables for the determination of thermodynamic properties of fluids. Usually, the steam tables are in an appendix in thermodynamic textbooks, and sometimes a few extra tables for different substances are also included. It should be made clear to the students that no published thermodynamics table is a direct transcript of experimental measurements, because such data must be smoothed, correlated, and made internally consistent by means of a mathematical model, *i.e.*, by an equation of state. Thus, thermodynamic tables can become obsolete as new data and improved fundamental EOSs become available. For carbon dioxide, several sources are available.<sup>[10,11,21,22]</sup>

## SOLUTION

Homogeneous fluids are normally divided into liquids and gases, but this distinction cannot always be sharply drawn because the two phases become indistinguishable at the critical point. Several authors<sup>[1-4]</sup> define the supercritical region as the region existing at temperatures and pressures above the critical temperature and critical pressure; this region is bounded by the dotted lines in Figure 1. For simplicity, in

this project we will use this definition of the supercritical state. The critical conditions for CO<sub>2</sub> are T<sub>c</sub> = 304.128 K, P<sub>c</sub> = 7.3773 MPa, and ρ<sub>c</sub> = 467.6 kg/m<sup>3</sup>. Thus, the isotherm at 360 K will be analyzed as supercritical for pressures above the critical pressure.

In this work, we use the Internet to obtain the predictions of the Span-Wagner EOS through the NIST webbook<sup>[11]</sup> and to obtain the predictions of the Peng-Robinson equation from Reference 16. We read the tables presented in the Appendix of Reference 1 for the Lee-Kesler model and also the tables presented in Reference 12 for pure carbon dioxide. Finally, we program the Soave-Redlich-Kwong EOS using the VisualBasic macro of Excel and use that program to show the results. This is only one of several possible lines of attack that students can choose to solve their assignment.

### Vapor-Liquid Equilibria Region

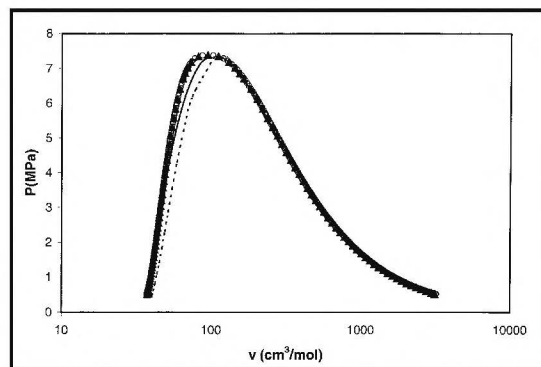
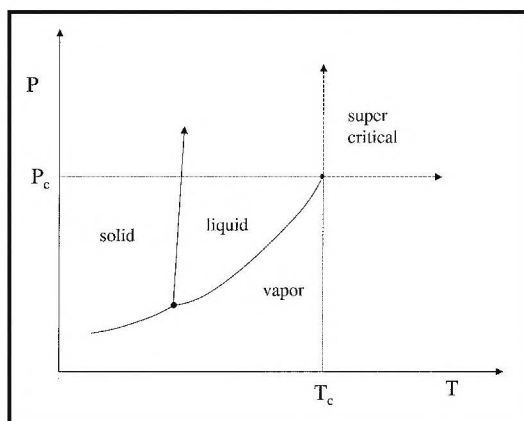
The phase envelope (vapor-liquid equilibria or saturation conditions) for carbon dioxide is shown in Figure 2. Results are shown for the Span-Wagner, Peng-Robinson, and Soave-Redlich-Kwong equations and also from the IUPAC tables. Results from the Lee-Kesler method are not shown because the available tables in Reference 1 (as well as in the original publication<sup>[9]</sup>) are provided only for the single phase (liquid or vapor). (The reason is that the Lee-Kesler method fails to predict a well-behaved van der Waals loop at near-critical temperatures, thus making it impossible to find two fluid states with the same fugacity; in normal practice, saturation pressures from the Lee-Kesler EOS are obtained from a separate linear correlation proposed by the same authors.<sup>[9]</sup>)

This figure illustrates the predictive capabilities of multiparametric equations of state. The Span-Wagner EOS is the equation most frequently used for carbon dioxide and can be taken as a reference (for a more detailed discussion, see References 10 and 11). On the scale of the graph, results from the IUPAC tables are equivalent. It is worth mentioning that tables,<sup>[11]</sup> software, and Internet<sup>[11]</sup> were used in this stage of the project, and they can also be used to show that “old” methods (tables) are not necessarily less accurate than “new” methods (Internet), or vice versa. Deficiencies of cubic equations of state in the critical region as well as in the prediction of liquid densities are shown by the SRK and PR results. For carbon dioxide, in the region under study, the PR equation is more accurate than SRK.

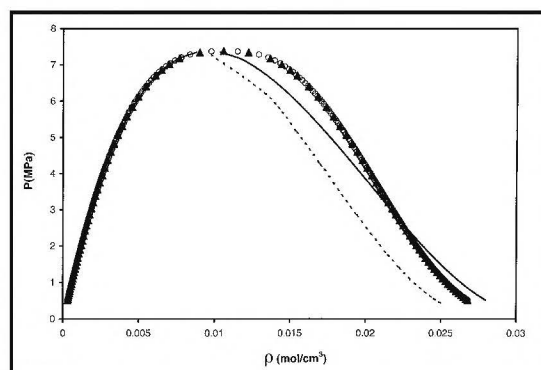
The phase envelope for carbon dioxide is also shown in Figure 3, but in a P-ρ diagram, which can be used to show the practical convenience of

**Figure 1.**

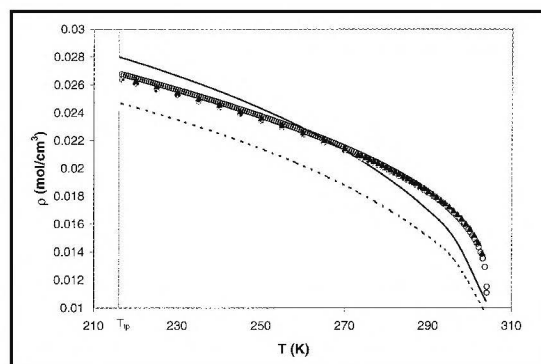
*PT diagram for a pure substance that contracts on freezing.*



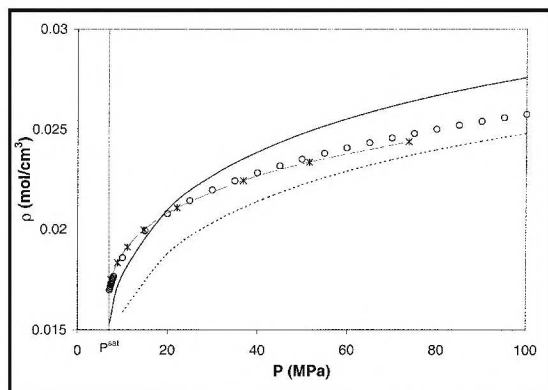
**Figure 2.** Vapor-liquid phase envelope for carbon dioxide shown as a P-v diagram. Continuous line predicted by the Peng-Robinson EOS,<sup>[6]</sup> dashed line predicted by the Soave-Redlich-Kwong EOS,<sup>[7]</sup> (○) predicted by the Span-Wagner EOS,<sup>[10]</sup> and (▲) predicted from the IUPAC tables.



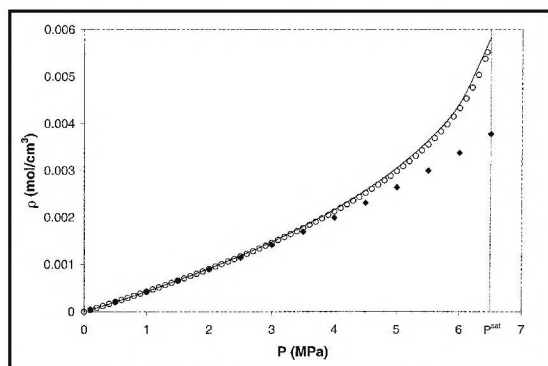
**Figure 3.** Vapor-liquid phase envelope for carbon dioxide shown as a P-ρ diagram. Continuous line predicted by the Peng-Robinson EOS,<sup>[6]</sup> dashed line predicted by the Soave-Redlich-Kwong EOS,<sup>[7]</sup> (○) predicted by the Span-Wagner EOS,<sup>[10]</sup> and (▲) predicted from the IUPAC tables.



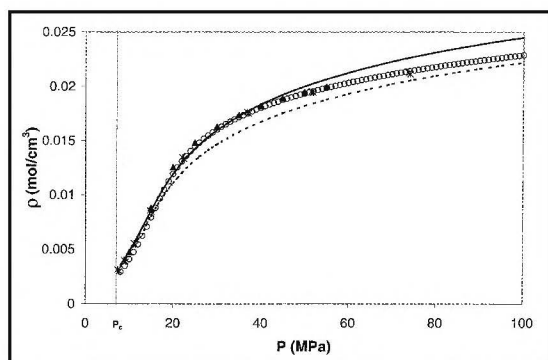
**Figure 4.** Saturated liquid density versus temperature diagram for carbon dioxide. Continuous line predicted by the Peng-Robinson EOS,<sup>[6]</sup> dashed line predicted by the Soave-Redlich-Kwong EOS,<sup>[7]</sup> (○) predicted by the Span-Wagner EOS,<sup>[10]</sup> (●) from the Rackett equation,<sup>[13]</sup> and (▲) from the modified Rackett equation due to Spencer and Adler.<sup>[14]</sup>



**Figure 5.** Density versus pressure diagram for carbon dioxide at 298.15 K, liquid phase. Continuous line predicted by the Peng-Robinson EOS,<sup>[6]</sup> dashed line predicted by the Soave-Redlich-Kwong EOS,<sup>[7]</sup> (○) predicted by the Span-Wagner EOS,<sup>[10]</sup> and (\*) from the corresponding states method (Lee-Kesler tables in [1]).



**Figure 6.** Density versus pressure diagram for carbon dioxide at 298.15 K, vapor phase. Continuous lines predicted by Peng-Robinson EOS,<sup>[6]</sup> (○) predicted by Span-Wagner EOS,<sup>[10]</sup> and (◆) predicted by virial equation (expanded in the density series and truncated at its second term).



**Figure 7.** Density versus pressure diagram for carbon dioxide at 360 K, a supercritical state. The continuous line is the Peng-Robinson EOS,<sup>[6]</sup> (○) is predicted by Span-Wagner EOS,<sup>[10]</sup> and (◆) is predicted by the virial equation (expanded in the density series and truncated at its second term).

working in terms of density. (Density is convenient to use because it always stays finite as  $P \rightarrow 0$ , whereas  $V$  diverges.<sup>[3]</sup>)

The Rackett equation<sup>[13]</sup> is a simple empirical equation for determination of saturated liquid volumes and relates them to the reduced temperature and the critical compressibility factor. Molar densities obtained from the original Rackett equation are shown in Figure 4 (closed gray circles); closed triangles represent the prediction from the modified Rackett equation due to Spencer and Adler.<sup>[14]</sup> Among the methods studied here, the modified Rackett equation gives the best prediction of saturated liquid densities.

### Liquid Phase

The density versus pressure diagram for carbon dioxide at 298.15 K is shown in Figure 5, from the saturation pressure (6.43 MPa) up to 100 MPa. Results are shown for the Span-Wagner, Peng-Robinson, and Soave-Redlich-Kwong equations and also from the corresponding states method (Lee-Kesler tables). Results from the IUPAC tables are not shown for clarity of the graph, but the results are equivalent to the Span-Wagner equation up to 60 MPa (range of validity of the IUPAC tables). This figure corroborated deficiencies of cubic equations of state in the prediction of liquid densities, as shown by the SRK and PR results. Prediction from the Lee-Kesler method is also shown in this figure, and good agreement with the Span-Wagner equation is obtained up to the range of validity of the tables (73.7 MPa or  $P_r = P/P_c = 10$ ).

### Vapor Phase

Except for the virial equation, all EOSs represent the saturated vapor region very well, as seen from Figures 2 and 3. In Table 1 we present the relative errors with respect to the Span-Wagner prediction for the two isotherms under study (278.15 and 298.15), from 0.51795 MPa (triple point) up to the vapor pressure at each temperature. Table 1 shows that all equations behave very well in the vapor phase, with an average error less than 2%, except the virial equation.

The virial equation (expanded in the density series and truncated at its second term) is often recommended<sup>[1-4]</sup> for use at low pressures (under 1 MPa). The results in Figure 6 show that for carbon dioxide at 298.15 K the virial equation can be used up to 2.5 MPa, with an error less than 2%. The PR EOS predictions are shown for comparison. The second virial coefficient was taken from the correlation due to Pitzer and Curl and presented in Reference 1.

### Supercritical State

The density versus pressure diagram for carbon dioxide at 360 K is shown

EOS/Temperature (K)	Virial	SRK <sup>[7]</sup>	PR <sup>[8]</sup>	LK <sup>[9]</sup>	IUPAC <sup>[12]</sup>
278.15 ( $P^{\text{sat}} = 3.9695$ MPa)	5	2.7	1.3	0.82	1.76
298.15 ( $P^{\text{sat}} = 6.4342$ MPa)	4.6	1.9	0.76	0.64	1.17

\* 
$$\sum_{n=1}^{N_p} \left( \frac{\rho_{\text{Span-Wagner}} - \rho_{\text{EOS}}}{\rho_{\text{Span-Wagner}}} \right)_{100}$$

in Figure 7, from the critical pressure up to 100 MPa. Results are shown for the same equations and methods presented for the liquid phase (Figure 5) corroborating the validity of the corresponding states method (Lee-Kesler tables) for carbon dioxide in the homogeneous phase up to the range of validity of the tables (73.7 MPa or  $P_r = P/P_c = 10$ ). Deficiencies of cubic equations of state in the prediction of liquid-like densities (high pressures) are shown by the SRK and PR results.

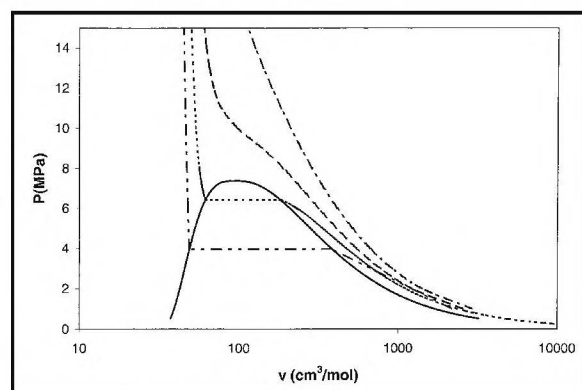
### The "Complete" $P$ - $v$ Diagram

The  $P$ - $v$  diagram for carbon dioxide predicted from the Span-Wagner equation is shown in Figure 8. The construction of this diagram is straightforward for the student from the NIST webpage.<sup>[11]</sup>

### FINAL COMMENTS

The results in Figures 2-7 can be used to discuss the advantages and deficiencies of the various methods. For example, Figure 3 can be used to discuss the deficiencies of cubic equations of state in the critical region as well as in the prediction of liquid densities, and Figure 5 can serve to show the importance of using a model within its range of validity; *e.g.*, if the IUPAC tables are extrapolated to 100 MPa (results not shown), errors up to 200% can be found.

Care must be taken to emphasize that although it is possible to draw conclusions about the best EOS for  $\text{CO}_2$  (or any other substance) for a given property and range of state conditions, such conclusions cannot be extended to other fluids, properties, or state conditions without further calculations. Thus, although the PR equation is found to be superior to the SRK equation for  $\text{CO}_2$  properties studied here, quite different conclusions may be drawn for another fluid. For this purpose,



**Figure 8.** Carbon dioxide  $P$ - $v$  diagram predicted by Span-Wagner EOS.<sup>[10]</sup> The continuous line represents the vapor-liquid phase envelope. The dotted-dashed line is the 360 K isotherm, the dashed line is the 320 K isotherm, the dotted line is the 298.15 K isotherm, and the double-dotted dashed line is the 278.15 K isotherm.

different substances can be assigned to each student, or results for other substances/regions can be shown in class.

### ACKNOWLEDGMENTS

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