Fixed-point Iteration Formulas from Cubic Equations of State, Useful in the Classroom and the Industry

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***Abstract*– A set of fixed-point iteration formulas v=g(v) was developed for the Van der Waals (VdW), Redlich-Kwong, Soave-Redlich-Kwong (SRK) and Peng-Robinson cubic equations of state (CEoS). These formulas allow the fast calculation of saturated specific volumes and vapor pressures, among other properties; moreover, they have been used in the classroom and have practical Chemical Engineering applications. The formulas were numerically verified using the VdW and SRK CEoS, and then applied to calculations in the two-phase, low-pressure, supercritical, and near-critical regions. Examples involving difficulties due to slow convergence or numerical machine limitations are presented.**

***Keywords*-- Thermodynamics, Equations of State, Computational Tools, Numerical Methods.**

I. Introduction

Chemical engineers widely use cubic equations of state (CEoS) in such areas of the process industry as equipment design and simulation, to calculate non-ideality corrections for gases and vapors. For example, CEoS are used for petroleum reservoir calculations, as well as estimating critical properties of polymer-solvent mixtures [1, 2]. Students from the Industrial Bioprocess Engineering Program at Universidad Nacional, Costa Rica apply CEoS at their Thermodynamics course for the design of compression refrigeration cycles. Other properties can be determined with these volumes, such as fugacities and vapor pressures [3, 4, 5]. One representative example of a CEoS is the Van der Waals equation of state, a relationship between pressure P, temperature T and specific volume v, where R is the universal ideal gas constant and a, b are specific constants of the fluid, shown here as equation (0) for informative purposes:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \qquad (0)$$

While the calculation of pressure is direct, calculating the specific volume with a CEoS involves solving a third-order polynomial. The resulting equation has three roots in the two-phase region, i.e., three values for the specific volume. The largest root is related to the saturated vapor, the smallest one is related to the saturated liquid and the one in between has no physical meaning [6]. A faster, easier to understand method to solve CEoS for the specific volume became necessary for the course, but also a means to teach the basics of numerical root-finding methods to Engineering students. One example of a JavaScript-based program was made elsewhere for the same purpose [7], although the author did not explain his method of solution[1].

Various techniques may be used to solve the cubic polynomial in v. Previous authors have discussed the algebraic solution (Cardan's formula), the Newton-Raphson method and variants, Padé interpolation, and the bisection method [8, 9, 10, 11, 12]. Other authors have discussed the existence of non-physical roots and the mathematical criteria to determine the phases that correspond to the physical roots [6, 8, 10, 12, 13]. At least two authors have discussed fixed-point iteration from a mathematical view, without reference to obtaining the iteration formula from the equation of state itself [11, 14]. One Thermodynamics textbook proposed two fixed-point iteration formulas to calculate specific volumes [15].

The present study is oriented to develop improved fixed-point iteration formulas from the CEoS themselves, both fast and robust, to obtain the vapor and liquid saturated specific volumes of pure substances. These formulas have been used successfully by the author in the classroom since they facilitate students the fast calculation of saturated specific volumes, among other uses. Students can understand the fixed-point iteration method with no previous exposure to Numerical Analysis topics, thus becoming familiar with CEoS by manipulating the equation of state itself to obtain the formulas.

II. THE PROPOSED METHOD

The fixed-point iteration method allows one to find the roots of a function $f(v) = 0$. It consists of rewriting the function in the form $v = g(v)$ and to iterate from an initial value v_0. The key is to find a form of the function $g(v)$ that converges to the expected root, as the iteration might be divergent, or else it may converge to a different root. The author is aware of the mathematical criteria to determine convergence, which involve contracting functions and differentiating $g(v)$ [16]. Fifteen formulas were initially developed and tested for the Van der Waals equation of state, a typical CEoS that is still relevant today [17]. The iterations were carried out in a spreadsheet (Microsoft© Excel), using as initial value $v_0 = {RT}/{P} = v_{ideal\ gas}$ for the saturated vapor specific volume and $v_0 = b$ for the saturated liquid specific volume. Full iterations were performed, not only to determine convergence, but to locate the root when the formula converges. The best three formulas were selected from the available ones, in terms of the number of required iterations for convergence.

[1] A working webpage is available at https://pjb10.user.srcf.net/thermo/

Equivalent equations were developed for typical CEoS, such as the Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson, which are presented here. A list of all the generated formulas is included in Tables A1 and A2. of the Supplementary Information. Calculations and benchmarking results are included in Table A4 of the Supplementary Information.

III. SELECTED FORMULAS

The recommended equations are (Eq. 1) for saturated vapor, (Eq. 2) for saturated liquid and (Eq. 3) for both saturated vapor and saturated liquid. These results were verified using a similar set of formulas obtained from the Soave-Redlich-Kwong CEoS. The results are shown in Table A5 of the Supplementary Information; they are comparable to the results in Table A4. The following are the recommended equations, as indicated above, for all the CEoS considered in this study, being some of the most used in academia and industry. Related equations from different CEoS are distinguished as 1, 1', 1'' and 1'''. When applicable, two versions of the same equation with the same fast convergence are labeled with (a) and (b).

Van der Waals (VdW):

$$v = b + \frac{RT}{P + \frac{a}{v^2}} \tag{1}$$

$$v = \frac{RTv}{P(v-b)} - \frac{a}{Pv} \tag{2}$$

$$v = b\left[1 - \frac{RTv}{Pv^2 + a}\right]^{-1} \tag{3}$$

Redlich-Kwong (RK):

$$v = b + \frac{RT}{P + \frac{a}{T^{1/2}v(v+b)}} \tag{1'}$$

$$v = \frac{RTv}{P(v-b)} - \frac{a}{T^{1/2}P(v+b)} \tag{2a'}$$

$$v = \frac{RT(v+b)}{P(v-b)} - \frac{a}{T^{1/2}Pv} - b \tag{2b'}$$

$$v = b\left[1 - \frac{RT^{3/2}(v+b)}{PT^{1/2}v(v+b) + a}\right]^{-1} \tag{3'}$$

Soave-Redlich-Kwong (SRK):

$$v = b + \frac{RT}{P + \frac{a\lambda}{v(v+b)}} \tag{1''}$$

$$v = \frac{RTv}{P(v-b)} - \frac{a\lambda}{P(v+b)} \tag{2a''}$$

$$v = \frac{RT(v+b)}{P(v-b)} - \frac{a\lambda}{Pv} - b \tag{2b''}$$

$$v = b\left[1 - \frac{RT(v+b)}{Pv(v+b) + a\lambda}\right]^{-1} \tag{3''}$$

Peng-Robinson (PR):

$$v = b + \frac{RT}{P + \frac{a\alpha}{(v^2 + 2bv - b^2)}} \tag{1'''}$$

$$v = \frac{RT\left[v - (\sqrt{2}+1)b\right]}{P(v-b)} - \frac{a\alpha}{P\left[v + (\sqrt{2}-1)b\right]} + (\sqrt{2}+1)b \tag{2a'''}$$

$$v = \frac{RT\left[v + (\sqrt{2}-1)b\right]}{P(v-b)} - \frac{a\alpha}{P\left[v - (\sqrt{2}+1)b\right]} - (\sqrt{2}-1)b \tag{2b'''}$$

$$v = b\left[1 - \frac{RT(v^2 + 2bv - b^2)}{Pv(v^2 + 2bv - b^2) + a\alpha v}\right]^{-1} \tag{3'''}$$

IV. APPLICATION EXAMPLES

Example 1 – Two-phase region

The obtained equations were tested for a typical point in the two-phase region of butane, as seen in Table 1.

TABLE 1: Parameters for the study

Substance: n-butane
Critical pressure, P_c: 3,796 Mpa
Critical temperature, T_c: 425,1 K
R = 8,314 MPa cm^3 mol^{-1} K^{-1}
Test temperature = 298,15 K
Test pressure = 2,43 bar

Source: Smith et al., 2007

Saturated specific volumes were calculated from the data of Table 1 using the formulas above, these results were compared to the experimental values [18] and other values obtained from a reference equation of state [19]. Iterations were made on a spreadsheet by merely copying and pasting cells; they were very fast for any number of iterations. Results are shown in Table 2, being the Peng-Robinson CEoS result the closest to the experiment. These results can be verified by any other available method (such as Cardano's or Newton's methods).

Example 2 – Supercritical and near-critical regions

The vapor specific volume was calculated for supercritical carbon dioxide at 310 K and 75 bar, using the formulas above, and compared to the experimental value [20]. At this state, all equations converge to the same root. The chosen state is near the critical point, so the convergence became very slow.

Table 2: Comparison of saturated specific volumes, Example 1

Source	Liquid specific volume, cm^3/mol	Vapor specific volume, cm^3/mol
Experimental (Haynes & Goodwin, 1982)	101,50	9409,0
NIST Fluid Properties (reference EoS)	106,19	9855,7
Van der Waals*	164,44	9737,6
Redlich-Kwong*	112,75	9571,5
Soave-Redlich-Kwong*	109,37	9520,9
Peng-Robinson*	96,57	9488,4

(*) Own source, based on the methods proposed in this work

TABLE 3: Comparison of saturated specific volumes, Example 2

Source	Vapor specific volume, cm^3/mol
Experimental (Elliot & Lira, 2012)	171,6
Van der Waals*	180,5
Redlich-Kwong*	174,4
Soave-Redlich-Kwong*	179,0
Peng-Robinson*	169,2

(*) Own source, based on the methods proposed in this work

A standard acceleration method (Aitken-Steffensen) was applied to the obtained sequence of values to overcome the slow speed [21]. Another acceleration method (Wegstein method as per [22]) was implemented with identical results. This method can be easily repeated on successive sequences using a spreadsheet, as required to accelerate convergence. The results are shown in Table 3, and the Peng-Robinson CEoS result is closest to the experiment.

Example 3 – Low-temperature, very low-pressure region

Zhi & Lee [23] have reported than the analytical or algebraic method (i. e., Cardano's formula) fails when calculating saturated volumes in the low-temperature and very low-pressure liquid region, giving irrational results. This failure occurs due to machine arithmetic issues and not because of the CEoS themselves. The researchers used the Peng-Robinson CEoS in their work, and Equation (1''') from the present study converges rapidly to values almost identical to the ones reported by them. The difference is probably due to the values of the critical properties that were used [24, 25], but not published by the authors. The results are shown in Table 4.

Example 4 – Liquid and vapor saturation curves for water

The saturated curves in the Pv diagram for water were easily obtained and plotted in Figure 1 below, using the Peng-Robinson CEoS and the methods developed in this work. The resulting curves were compared to saturated temperature and pressure values from the steam tables [26]; the latter data come from a reference equation and differ from the ones obtained if the Maxwell equal-area relationship [4, 5] is applied to the CEoS.

TABLE 4: Comparison of saturated specific volumes, Example 3

Compound @ T, P	Experimental	P-R (Cardano formulas)	P-R (Newton-Raphson)	(Eq. 1''')
Propene at 87,9 K and 9,18E-10 MPa	55,07	1002,6	53,91	53,907
1-butene at 87,8 K and 3,56E-13 MPa	70,09	1671,6	70,37	70,358
1-pentene at 107,93 K and 4,48E-12 MPa	86,64	1946,1	89,11	89,097

Volumes in cm^3/mol

Sources: Zhi et al. (2002); Daubert et al., 1988; Reid et al., 1977; own source

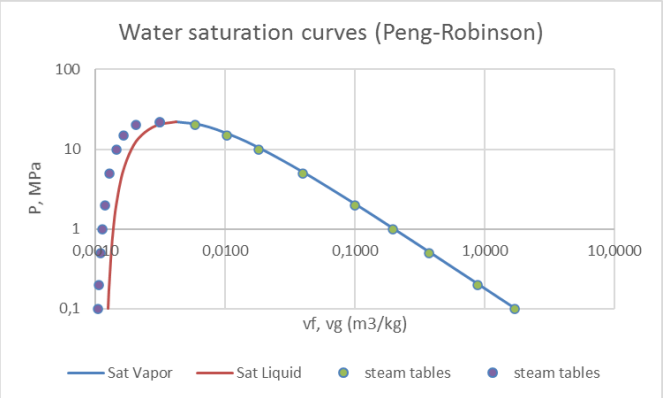

FIGURE 1. Water saturation curves, Example 4.
Sources: Cengel et al, 2015; own work.

The adjustment between the calculated saturated vapor specific volumes and the steam tables values is quite good. Such alignment may still be improved using some of the spreadsheet tools (e. g. Goal Seek, Solver), but the saturated pressure values would change. There are techniques to improve the calculated saturated liquid volumes, which can be used with any CEoS [27]. It is suggested to implement the Maxwell equal-area relationship in a future study.

V. Analysis and Discussion

Three desirable properties of any numerical root-finding method are convergence, robustness and stability. There are formal mathematical definitions of these terms but, for the purpose of this document, "convergence" means that each successive value or iteration is nearer to a defined limit, which is one root of the function; "robustness" means that the method converges to the same root for different initial values; "stability" means that the method does not magnify errors -for example, due to the experimental nature of the input variables-. Moreover, "linear convergence" is one type of convergence where the logarithm of the error shows a linear relationship with respect to the number of iterations.

Both convergence and robustness of the proposed method were tested using Equation (1'') along with the Soave-Redlich-Kwong (SRK) CEoS. The vapor specific volume was calculated for supercritical n-butane at 510 K and 25 bar, at this state there is only one root. Initial values of $v_0 = v_{ideal\ gas} = 1696\ cm^3/mol$ and $v_0 = b = 80{,}667\ cm^3/mol$ were used respectively.

Convergence and robustness of the method are shown in Figure 2 below, where the root $v = 1486{,}195\ cm^3/mol$ is obtained from two very different initial values; the stability of the method is also implied in these results. The linear convergence is shown in Figure 3 below, where the differences between successive values of the specific volume are plotted against the number of iterations. These differences approach zero as a limit when the number of iteration increases, and they show a linear trend when plotted on a semi-logarithmic scale.

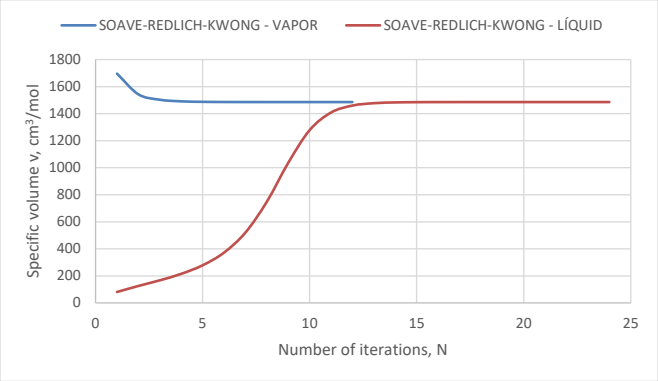

FIGURE 2. *Convergence and stability of the method, SRK CEoS. Own source.*

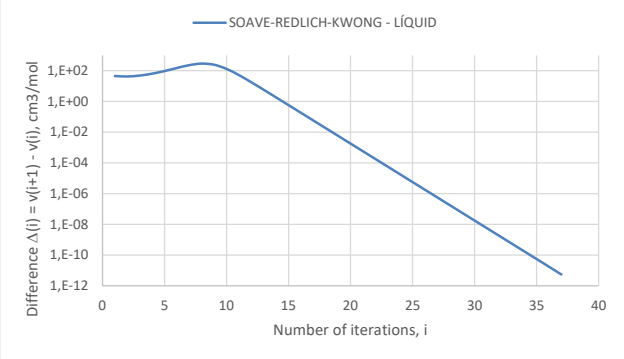

FIGURE 3. Linear convergence of the method, SRK CEoS. Own source.

The convergence of the method allows one to define a termination criterion once the difference between consecutive values reaches a specified tolerance. Linear convergence also means that the method requires approximately double number of iterations than the quadratically-convergent Newton-Raphson approach.

VI. Conclusions and Recommendations

Three fixed-point iteration formulas were obtained for the Van der Waals, Redlich-Kwong, Soave-Redlich-Kwong, and Peng-Robinson cubic equations of state, respectively; they have been used to determine saturated liquid and vapor specific volumes. These formulas were successfully tested for several state conditions, showing stability, robustness, and convergence. They were proven to be useful in the classroom, as an aid for the students to comprehend CEoS and root-finding numerical methods. The formulas can be also applied to the calculation of vapor pressure, compressibility, and critical properties.

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Supporting Information – Appendix A

A document detailing the iterative formulas, its development and the iterations results is available to download. One spreadsheet, with the calculations for the iterative formula benchmarking and the implementation of the examples, is also available upon request.

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