

Estimating Real-Gas Heat Capacities Using Cubic Equations of State: An Undergraduate Chemical Engineering Thermodynamics Case Study with CO₂

Shashi B. Lalvani

Chemical, Paper and Biomedical Engineering, Miami University, Oxford, OH 45056

Email: lalvansb@miamioh.edu

Abstract

This paper demonstrates the use of equations of state (EOS) for determining the constant-pressure and constant-volume heat capacities (C_p , C_v) as a classroom experience. Typical undergraduate thermodynamics courses often emphasize ideal-gas behavior and phase equilibria more than caloric properties. Non-ideal gas EOS, namely the van der Waals (vdW) and Redlich-Kwong (RK) are employed in the study and serve as density-dependent departure functions. An ideal-gas polynomial correlation was used to provide the temperature dependence of the heat capacity. The thermodynamical relation involving the relationship between P , V and T were used to compute heat capacity of carbon dioxide at 400 K. The Wagner/NIST EOS (via CoolProp) serve as highly accurate and standard benchmarks. RK predicts both C_p and C_v within 2-22% up to 160 bar, whereas vdW deteriorates to 2-26% error and consistent with its analytic structure-predicts no volume dependence of C_v . The case study illustrates how cubic EOS behavior can be used to predict caloric properties and provides a learning experience for undergraduate thermodynamics students.

Keywords: Heat capacity, Equation of State, van der Waals, Redlich-Kwong

I. Introduction

Undergraduate chemical engineering thermodynamics courses introduce students to ideal-gas behavior, cubic equations of state, and the relationships among internal energy, enthalpy, and PVT properties. However, the estimation of real-gas heat capacities is often left to advanced electives or graduate courses. This article bridges that gap by demonstrating a complete, analytically transparent method for estimating real-gas caloric properties using tools already familiar to undergraduates.

Two ingredients are required:

1. Ideal-gas heat capacity correlation using the classical four-parameter polynomial involving temperature dependence at zero density given below, and

$$C_p^{ig}(T) = R(A + BT + CT^2 + \frac{D}{T^2}) \quad (1)$$

2. Equation of states (EOS) supplying density dependence and corresponding departure functions.

Carbon dioxide (CO₂) is chosen because its critical properties are well known, its real-gas behavior is moderate, and high-accuracy reference data are available and provides for accurate thermodynamic surface (Span–Wagner, 1996). Coefficients were fit to NIST-JANAF data from 100-1000 K. At 400 K.

II. Materials and Methods

The coefficients A , B , C , D in equation (1) were obtained here by a least-squares fit of this form to the NIST–JANAF Thermochemical Tables values for CO₂(g) at $T = 100$ – 1000 K (Table 1). The fit reproduces the JANAF

C_p values to within 1.5% over 100–1000 K; at $T = 400$ K it gives $C_p^{ig} = 42.12 \text{ J mol}^{-1}\text{K}^{-1}$, matching the JANAF value of $41.33 \text{ J mol}^{-1}\text{K}^{-1}$ to within 1.91%, and consequently $C_V^{ig} = C_p^{ig} - R = 32.68 \text{ J mol}^{-1}\text{K}^{-1}$.

Table 1. NIST-JANAF C_p^{ig} data used to fit the ideal-gas polynomial (CO_2 , gas).

T (K)	100	200	298.15	300	400	500	600	700	800	900	1000
C_p^{ig} (J/mol·K)	29.94	34.47	38.45	38.65	42.12	45.21	47.78	49.95	51.79	53.32	54.62

A. Cubic Equations of State

Cubic EOS are central to undergraduate thermodynamics because they provide closed-form algebraic expressions, simple parameterization using only T_c and P_c , and reasonable accuracy near the critical point.

Van der Waals (VdW)

It was chosen because of historical importance and usually well-known to students beside the ideal gas law, however, it is structurally limited as the attraction term (a/v^2) does not include temperature dependence.

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad a = \frac{27}{64} \frac{R^2 T_c^2}{P_c}, \quad b = \frac{RT_c}{8P_c} \quad (2)$$

For CO_2 ($T_c = 304.13 \text{ K}$, $P_c = 73.77 \text{ bar}$) these give $a = 3.592 \frac{\text{L}^2 \text{atm}}{\text{mol}^2}$, $b = 0.04267 \frac{\text{L}}{\text{mol}}$

Redlich-Kwong (RK)

Introduces a temperature-dependent attraction term $a/\sqrt{T}$, improving vapor-pressure and caloric predictions.

$$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)} \quad a = \frac{0.42}{P_c} \frac{R^2 T_c^{2.5}}{P_c}, \quad b = \frac{0.08664 RT_c}{P_c} \quad (3)$$

For CO_2 ($T_c = 304.13 \text{ K}$, $P_c = 73.77 \text{ bar}$) these give $a = 6.45 \frac{\text{L}^2 \text{atmK}^2}{\text{mol}^2}$, $b = 0.0297 \frac{\text{L}}{\text{mol}}$

B. Estimating C_v from Departure Functions

A standard thermodynamic identity relates the volume dependence of C_v to the second temperature derivative of pressure:

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad \text{or} \quad C_v(T, V) = C_v^{ig}(T) + \int_{\infty}^V T \left(\frac{\partial^2 P}{\partial T^2}\right)_V dV \quad (4)$$

vdW Prediction

Because vdW pressure is linear in temperature:

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0 \quad \text{Thus:} \quad C_v^{vdW}(T) = C_p^{ig}(T) \quad (5)$$

RK Prediction

The $a/\sqrt{T}$ term produces nonzero curvature:

$$C_v^{RK}(T, V) = C_v^{ig}(T) - \frac{3a}{4bT^{3/2}} \ln\left(\frac{V}{V+b}\right) \quad (6)$$

Estimating C_p from the Mechanical Relation:

$$C_p - C_v = -T \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T \quad \left(\frac{\partial V}{\partial T}\right)_P = -\frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T} \quad (7)$$

The above equation links caloric and mechanical properties. Because it depends only on first derivatives, it is less sensitive to EOS limitations than the C_v departure integral. Thus:

$$C_p^{vdW} - C_v^{vdW} = -T \frac{\left(\frac{R}{V-b}\right)^2}{\frac{RT}{(V-b)^2} + \frac{2a}{V^3}} \quad (8)$$

RK Prediction

In a similar fashion, the following expression is obtained:

$$C_p^{RK} - C_v^{RK} = -T \frac{\left[\frac{R}{V-b} + \frac{a}{2} T^{-3/2} \frac{1}{V(V+b)}\right]^2}{\frac{RT}{(V-b)^2} + \frac{a}{\sqrt{T}} \frac{2V+b}{V^2(V+b)^2}} \quad (9)$$

The above are full vdW and RK expressions for $C_p - C_v$ in terms of T and V. The analytical approach was adopted to obtain the differential the EOS, integration of the C_v -departure integrand, and simplification of $(C_p - C_v)$ to eliminate manual error, then converted to numerical functions. For each pressure P on the T = 400 K isotherm, the appropriate cubic equation was solved for the single physically relevant (vapor/supercritical) root V (T, P); C_v , $C_p - C_v$, and hence C_p were then evaluated at that state point. Reference “measured” values of C_p , C_v , and V were generated at the same (T, P) points from the Span–Wagner reference equation of state for CO₂ (Span & Wagner, 1996), implemented in the open-source CoolProp library, which reproduces the NIST fluid property surface to experimental accuracy and is used here in lieu of a laboratory data set.

T = 400 K was selected deliberately: it lies safely above CO₂'s critical temperature (304.13 K), so the entire pressure range explored is single-phase, avoiding the vapor–liquid dome and the associated singular behavior of C_p near the critical locus, while still spanning compressibility factors Z from 1.00 down to about 0.70 - a substantial, and analytically tractable, real-gas regime.

C. Results and Discussion

Reference values were generated using the Span-Wagner EOS via CoolProp.

A. C_p as a function of pressure

Figure 1 shows that all curves coincide with low pressure, where the gas behaves ideally, and diverge progressively as pressure increases. The Redlich–Kwong curve tracks the reference data closely up to 40-60 bar; the van der Waals curve is systematically too low, understating the true C_p by up to 26% at 160 bar.

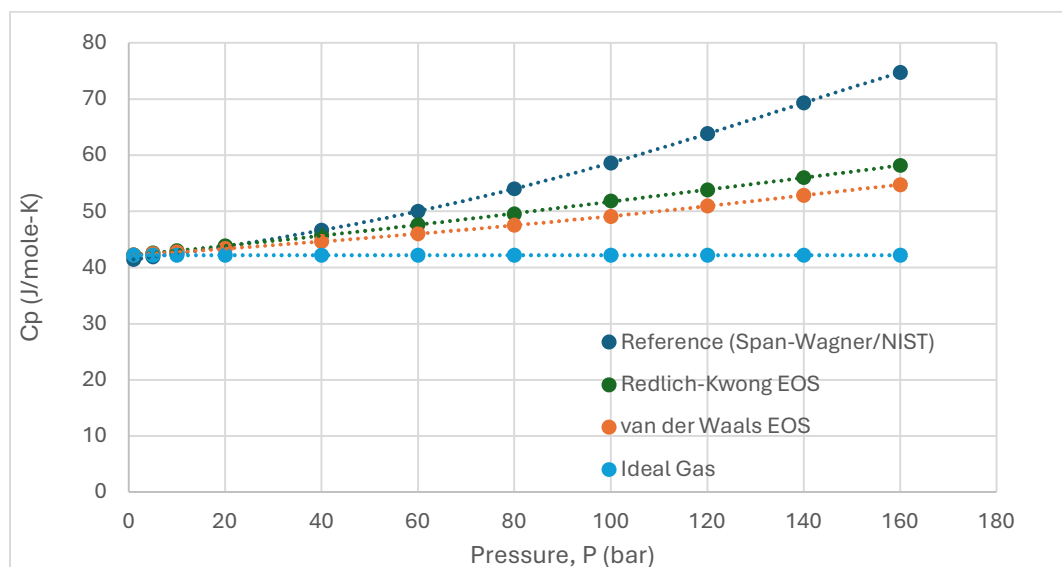


Figure 1. C_p of CO_2 at 400 K vs. pressure

B. C_V as a function of molar volume

Figure 2 highlights the structural difference between the two models (equations 5 and 6). The van der Waals curve is a horizontal line at the ideal-gas value $C_V^{ig} = 33.9 \text{ J mol}^{-1}\text{K}^{-1}$ for every volume, because $\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$ for that equation of state. The Redlich–Kwong curve, by contrast, rises as the gas is compressed (i.e., decrease in volume), and follows the reference curve’s shape and magnitude far more closely, though it too under-predicts the reference C_p at small V . At 1 bar, all pressure/volume-dependent corrections vanish and the estimated C_p , C_V reduce to the ideal-gas polynomial of Eq. (1) (within numerical rounding); the residual 1% mismatch there versus the reference reflects only the imperfect fit of that polynomial to the true ideal-gas curve and is common to every model. All growth in error beyond that baseline, as pressure increases, is attributable entirely to the choice of equation of state.

Redlich–Kwong is uniformly better than van der Waals, most dramatically for C_V . This is a direct, analytically traceable consequence of equation 6: van der Waals has zero curvature of P with respect to T , so it is structurally independent of volume

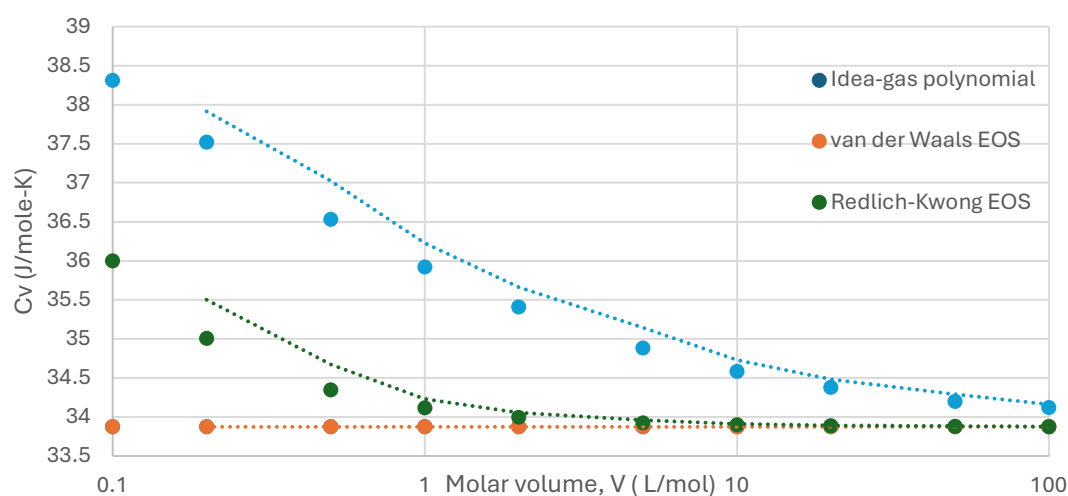


Figure 2. C_V of CO_2 at 400 K vs. molar volume (log scale).

dependence into C_V , regardless of how well its a and b constants are fitted. Redlich–Kwong's $a/\sqrt{T}$ temperature dependence, added purely to improve vapor-pressure predictions when the equation was originally proposed, turns out to also supply exactly the missing curvature needed for a qualitatively correct $C_V(V)$ trend.

C. $C_P - C_V$ from the mechanical relation

Unlike the individual C_P and C_V curves, the difference $C_P - C_V$ computed from the two cubic equations (Eqs. 8 & 9) of state agree closely with each other over most of the range, and both track the reference curve reasonably well up to about 80 bar, after which the reference curve (which reflects the true, more strongly curved PVT surface of CO_2) pulls away modestly. This shows that the mechanical $\left(\frac{\partial V}{\partial T}\right)_P$ and $\left(\frac{\partial P}{\partial V}\right)_T$ derivatives that enter

$C_P - C_V$ are less sensitive to the crudeness of the attraction term than the C_V -departure integral itself, which is dominated by the second temperature derivative $\left(\frac{\partial^2 P}{\partial T^2}\right)_V$ – identically zero for van der Waals. $C_P - C_V$ is a more forgiving quantity to estimate than C_P or C_V separately. Because the mechanical relation of equation (7) depends on $\left(\frac{\partial P}{\partial V}\right)_T$ and $\left(\frac{\partial P}{\partial T}\right)_V$ – first derivatives that both cubic equations reproduce reasonably well – rather than on $\left(\frac{\partial^2 P}{\partial T^2}\right)_V$, the two models agree much more closely with each other and with the reference for $C_P - C_V$ (Figure 3) than they do for C_V alone (Figure 2). This is a useful diagnostic in practice: an equation of state can give a passable $C_P - C_V$ while still being quite wrong about how that difference is split between C_P and C_V .

The magnitude of the errors found here (a few percent to 22% for Redlich–Kwong, up to 2–26% for van der Waals, at pressures approaching half the critical pressure) is consistent with the general engineering experience that cubic equations of state, calibrated only to the critical point, are adequate for quick estimates but are not a substitute for a multiparameter reference equation (such as Span–Wagner) when accurate caloric properties are required near or above roughly half the critical pressure.

D. Compressibility factor and error summary

Figure 4 shows why the heat-capacity errors grow with pressure: as Z departs further from unity, both cubic equations of state increasingly misestimate the molar volume at a given (T, P) , and van der Waals systematically over-predicts the non-ideality (lower Z , i.e. more compressed volumes than are physically observed), consistent with its underestimation of C_V and C_P .

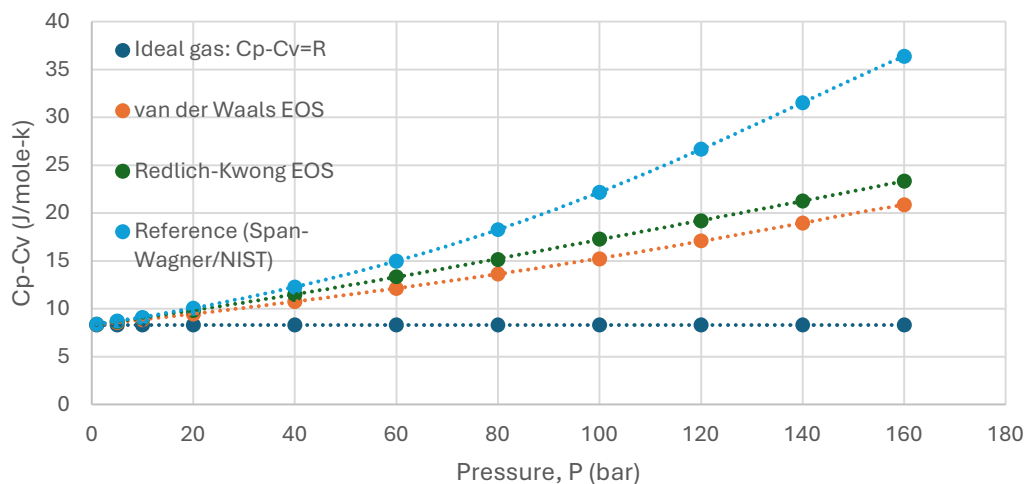


Figure 3. $C_P - C_V$ of CO_2 at 400 K

Figure 5 shows that the heat capacity errors with respect to the Span–Wagner reference, increase with pressure especially for the case of van der Waals equation of state as compared to the RK. In the case of former, 11% and

26% error in C_V and C_P values are observed, while less error (9% and 22%, respectively) is found in the case of latter results obtained using the RK equation of state.

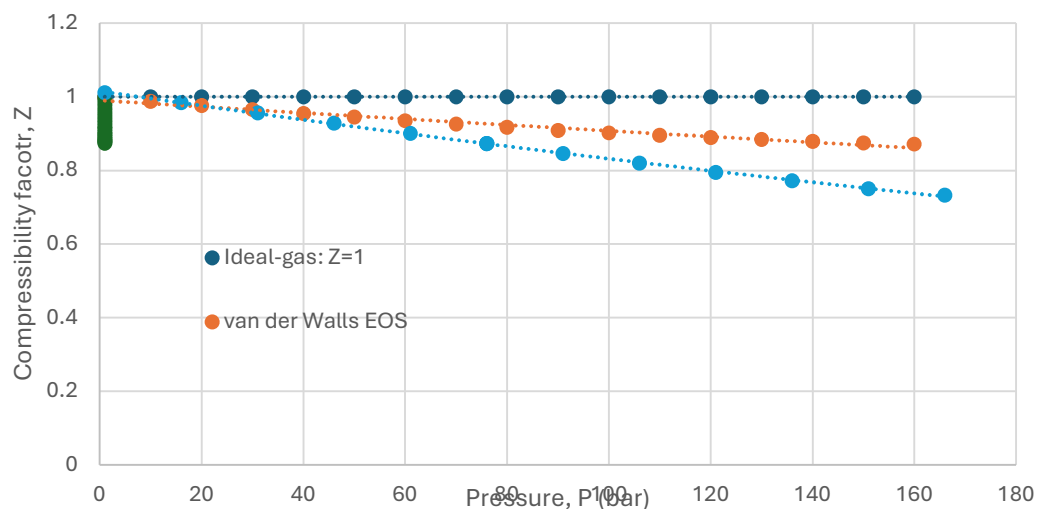


Figure 4. Compressibility factor $Z = Pv/RT$ vs. P

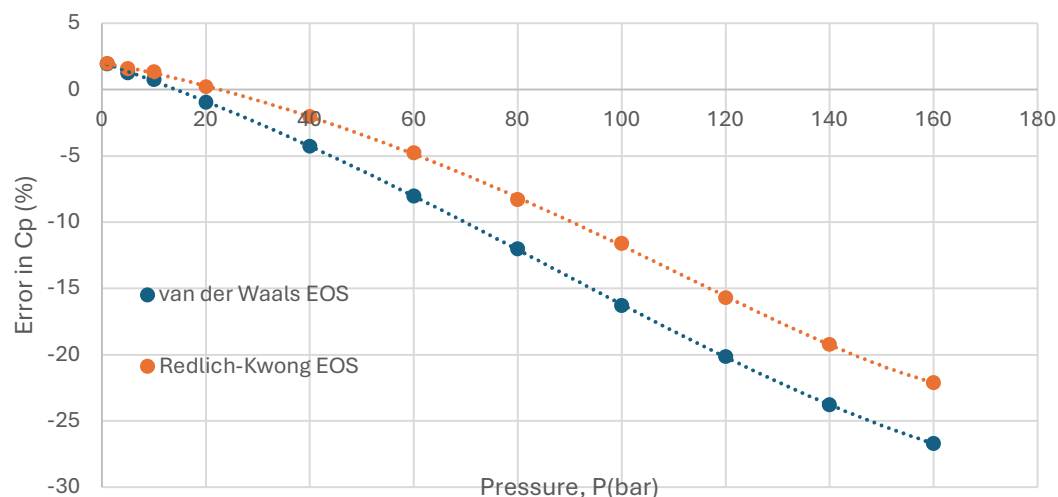


Figure 5a. Percentage error of the van der Waals and Redlich–Kwong estimates of C_p relative to the Span–Wagner reference

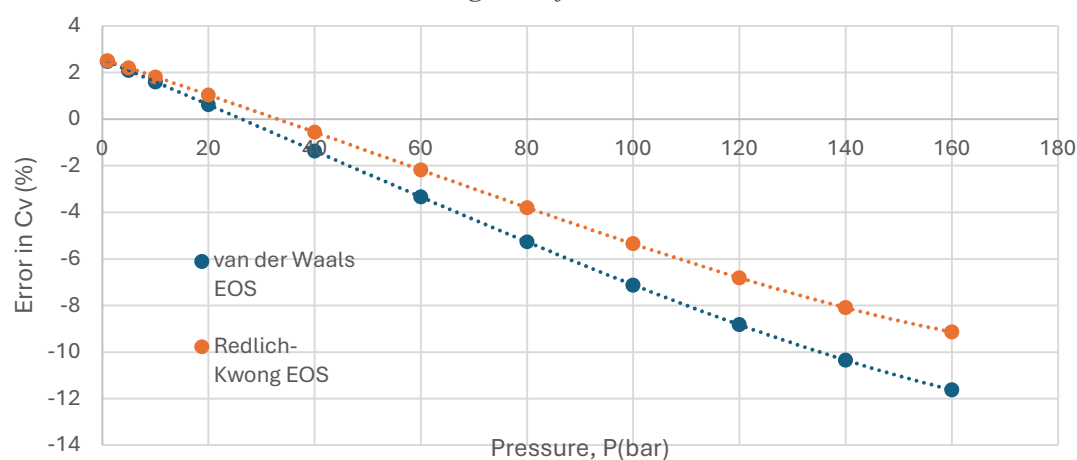


Figure 5b. Percentage error of the van der Waals and Redlich–Kwong estimates of C_v relative to the Span–Wagner reference

III. Conclusion

This article presents a complete, undergraduate-friendly study for estimating real-gas heat capacities using two cubic EOS. The Redlich-Kwong equation relatively performs better, while van der Waals performs poorly for caloric properties because of its structural limitations. The case study reinforces core thermodynamic concepts and demonstrates how cubic EOS connect PVT behavior to caloric properties.

References

1. Smith, J. M., Van Ness, H. C., Abbott, M. M. Introduction to Chemical Engineering Thermodynamics, 7th ed., McGraw-Hill.
2. NIST-JANAF Thermochemical Tables, CO₂.
3. Bell, I. H. et al. "CoolProp: An Open-Source Thermophysical Property Library." Ind. Eng. Chem. Res. (2014).
4. Redlich, O., Kwong, J. N. S. "On the Thermodynamics of Solutions." Chem. Rev. (1949).
5. Elliott, J. R., Lira, C. T. Introductory Chemical Engineering Thermodynamics, 2nd ed.
6. Prausnitz, J. M., Lichtenthaler, R. N., de Azevedo, E. G. Molecular Thermodynamics of Fluid-Phase Equilibria, 3rd ed.
7. Sandler, S. I. Chemical, Biochemical, and Engineering Thermodynamics, 5th ed.
8. Reid, Prausnitz & Poling. The Properties of Gases and Liquids.
9. Tester, J. W., Modell, M. Thermodynamics and Its Applications, 3rd ed.
10. NIST-JANAF Thermochemical Tables, Carbon Dioxide (CO₂), <https://janaf.nist.gov/tables/C-095.html>.
11. Span, R., Wagner, W., "A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa," J. Phys. Chem. Ref. Data, 25, 1509–1596 (1996).
12. Bell, I. H., Wronski, J., Quoilin, S., Lemort, V., "Pure and Pseudo-pure Fluid Thermophysical Property Evaluation and the Open-Source Thermophysical Property Library CoolProp," Ind. Eng. Chem. Res., 53 (6), 2498–2508 (2014).
13. Redlich, O., Kwong, J. N. S., "On the Thermodynamics of Solutions," Chem. Rev., 44 (1), 233–244 (1949).