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Square-Well Potential and a New α Function for the Soave–Redlich–Kwong Equation of State

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A new α function, based on the equality of the second virial coefficient from the Soave–Redlich–Kwong (SRK) equation of state (EoS) and the square-well (SW) potential, is derived to describe the supercritical behavior of the α function in the SRK EoS. To avoid anomalous behavior for predicting thermal properties near the critical point, the model parameters are obtained by equating the slope and curvature of the SW α function to the slope and curvature of Soave's α function at the critical point. The obtained SW α function is a monotonic decreasing function with temperature and becomes zero at a very high temperature. The SW α function was used with the SRK EoS to predict the second virial coefficient of gases, Boyle temperature, compressibility factor, fugacity, enthalpy, isobaric heat capacity, vapor pressure, and Joule–Thomson inversion curve for certain fluids; the agreement with experimental data and recommended values of IUPAC tables was found to be satisfactory especially at high temperatures. Consequently, the SW α function can be used with the SRK EoS at supercritical temperatures, while the original α function is still valid for the critical and subcritical temperatures.

Introduction

Since Soave¹ modified the Redlich and Kwong (RK) equation of state (EoS),² many new EoSs have been developed.³ In many applications, however, the Soave–Redlich–Kwong (SRK) EoS has been preferred to other EoSs. There are many reasons for this preference. The SRK EoS is simple in form and easy to use. It accurately predicts the fugacity of light compounds not only at high pressures but also at the critical point.⁴ At the critical point, it also accurately predicts the second virial coefficient of pure gases.⁵

The SRK EoS, in general, describes accurately the vapor–liquid equilibria of natural gas mixtures; i.e., it represents satisfactorily the fugacity of subcritical and supercritical components in a natural gas mixture. In other applications, e.g., at high temperatures, the SRK EoS poorly represents the supercritical behavior of some heavy and polar substances. This poor behavior is attributed to the inaccuracy of Soave's α function. In general, for a substance, an α function is a measure of attractive forces and a function of temperature. For instance, Soave's α function decreases, becomes a minimum at $T_r = (1 + 1/m)^2$, and then increases with temperature. However, this behavior poses some problems as suggested by Segura et al.⁶ As pointed out by Twu et al.,¹¹ an α function must be finite and positive for all temperatures, equals unity at the critical point, and approaches a finite value as the temperature approaches infinity.

Many α functions have been developed.^{3,7,8} These functions are mostly empirical; however, semiempirical α functions were also developed.^{9,10} While the parameters of α functions are usually determined by fitting the EoS to the vapor pressure of substances, the

extension to supercritical temperature is purely prediction. However, because of empiricism, this extrapolation should be accomplished with care.

Peng and Robinson¹² (PR) successfully used the Soave-type α function with their pressure–volume–temperature (PVT) relationship. The PR EoS has widely been used in the petroleum industry. Considering the retrograde condensation of gas condensate mixtures, Danesh et al.¹³ introduced an improved version of the PR EoS by proposing a different α function for the supercritical components of the gas condensate mixtures. In fact, Danesh et al.¹³ adjusted the parameter m in the α function of the PR EoS for the presence of supercritical components of gas condensate mixtures. Twu et al.^{14,15} proposed a new α function, which accurately predicts the vapor pressure of pure substances from the triple point to the critical point. For the supercritical part of their α function, they used the same form of the α function as they did for the subcritical part but with different coefficients by matching the α function of hydrogen and methane in the supercritical region to reproduce Henry's constants for these solutes in hydrocarbon liquids. Twu et al.^{14,15} also maintained the continuity of the prediction of caloric properties at the critical point by making sure that the departure from enthalpy and heat capacity is smooth at the critical point. Flöter et al.¹⁶ also improved the PR EoS for predicting the fluid-phase equilibria of high-pressure, high-temperature binary asymmetric mixtures by introducing a new α function for supercritical methane. For this purpose, they correlated a third-order polynomial α function by matching the predicted fugacity of methane to the recommended values of IUPAC tables.

The α functions from Danesh et al.¹³ and Flöter et al.¹⁶ are not continuous at the critical point, thus showing an anomalous behavior in predicting thermal properties at and near the critical point. The Twu et al.^{14,15} α function, though very accurate for predicting the vapor pressure, does not show any improvement for

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predicting thermodynamic properties in the supercritical region compared to Soave's α function. In fact, these α functions are empirical with no theoretical grounds. Few investigators also attempted to find theoretical α functions. Lee et al.⁹ developed an attractive pressure term using the SW potential function and a coordination number model. Nasrifar and Jalali¹⁷ showed that the Lee et al.⁹ EoS accurately predicts the *PVT* behavior; the prediction of saturated properties was not so good however. In fact, the Lee et al.⁹ EoS is not accurate for predicting saturated properties. Nasrifar and Moshfeghian¹⁰ sought an α function from the second virial coefficient and the SW potential function. They found it difficult to accurately correlate vapor pressure data and at the same time accurately predict the single-phase *PVT* of fluids for wide ranges of pressure and temperature.

In fact, Soave's α function is simple and reasonably accurate for predicting the vapor pressure of normal substances. Its deficiency at high temperatures, however, can be alleviated by introducing a new function. Because gas-phase *PVT* data at low pressure can simply be reduced by the second virial coefficient and a potential function, one may conversely use the second virial coefficient to describe the *PVT* of gases. In this work, on the basis of the SW potential, a new equation to describe the supercritical part of Soave's α function is developed. The SW potential function is a crude potential function, however, simple enough to derive a simple expression for the α function. This equation is joined to the original α function of the SRK EoS to form a two-part α function. While the original Soave α function can be used to subcritical and critical temperatures, the SW part of the α function is used to supercritical temperatures. No adjustable parameters are used for the SW part of the α function; however, the second virial coefficient of gases as a measure of gas imperfection and some thermodynamic properties are predicted accurately.

SRK EoS

The SRK EoS relates pressure to temperature and volume by

$$P = \frac{RT}{v-b} - \frac{a_C \alpha(T_r)}{v(v+b)} \quad (1)$$

$$b = 0.08664 \frac{RT_C}{P_C} \quad (2)$$

$$a_C = 0.42747 \frac{R^2 T_C^2}{P_C} \quad (3)$$

with

$$\alpha(T_r) = [1 + m(1 - \sqrt{T_r})]^2 \quad (4)$$

where P is the pressure, T is the temperature, v is the molar volume, R is the gas constant, b is the molar covolume, a_C is the attractive parameter, the subscripts C and r stand for the critical and reduced properties, respectively, and m is the negative value for the slope of eq 4 at the critical point:

$$\left(\frac{d\alpha(T_r)}{dT_r} \right)_C = -m \quad (5)$$

The curvature of eq 4 at the critical point is also of importance in predicting the global phase behavior of binary and multicomponent mixtures.¹⁸ Hence,

$$\left(\frac{d^2\alpha(T_r)}{dT_r^2} \right)_C = \frac{m(m+1)}{2} \quad (6)$$

The parameter m was correlated by Soave¹ in terms of the acentric factor:

$$m = 0.480 + 1.574\omega - 0.175\omega^2 \quad (7)$$

where ω is the acentric factor. As mentioned before, the SRK EoS reasonably predicts the vapor pressure of pure substances when eq 4 is used as the α function. However, its behavior at high temperature causes anomalies. To amend this behavior, on the basis of the SW potential, a new equation to describe the supercritical part of Soave's α function is developed.

SW Potential, Second Virial Coefficient, and a New α Function

The SW potential is unrealistic, however, simple enough to drive an α function and preserve the real characteristics of complex potential functions. It is expressed by¹⁹

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma < r < \lambda\sigma \\ 0 & \lambda\sigma < r \end{cases} \quad (8)$$

where $u(r)$ is the potential energy, σ is the size parameter, ϵ is the depth of the potential well, and λ is the range of the potential well. The second virial coefficient is related to the potential functions by¹⁹

$$B_2 = 2\pi N_A \int_0^\infty \{1 - \exp[-u(r)/kT]\} r^2 dr \quad (9)$$

where B_2 is the second virial coefficient, N_A is Avogadro's constant, and k is Boltzmann's constant. Inserting eq 8 into eq 9 yields

$$B_2 = b\{1 - (\lambda^3 - 1)[\exp(\epsilon/kT) - 1]\} \quad (10)$$

where b is the molar covolume ($2\pi N_A \sigma^3/3$). However, the second virial coefficient of the SRK EoS is expressed by

$$B_2 = b - \frac{a_C \alpha(T_r)}{RT} \quad (11)$$

Comparing eqs 10 and 11 and then incorporating eqs 2 and 3 lead to

$$\alpha(T_r) = 0.20268(\lambda^3 - 1) T_r [\exp(\epsilon/kT) - 1] \quad (12)$$

Equation 12 is an α function with two unknowns (λ and ϵ/k). When it is known that $\alpha(1) = 1$, only one of the unknowns can be independent. Then, one may be encouraged to correlate the α function with vapor pressure. Unfortunately, the SW α function cannot describe the vapor pressures as accurately as a Soave-type α function. The average absolute error would be

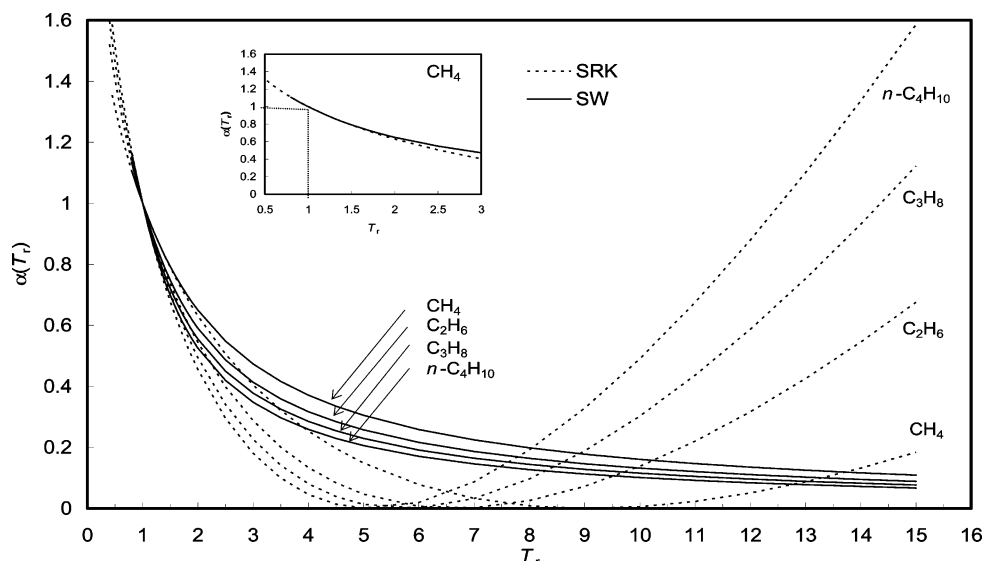


Figure 1. SW and Soave's α function as a function of the reduced temperature.

about 7%;¹⁷ the Soave-type α function correlates within 2% of experimental data, however. Then, we were interested in taking advantage of both α functions by using Soave's α function for the subcritical region and the SW α function for the supercritical region. To avoid anomalies in predicting caloric properties at and near the critical point, the two functions should be continuous and should have the same curvature at the critical point. These constraints cannot be met with eq 12 having only one independent unknown. To seek a solution, eq 12 is expanded to get the SW α function in a series form:

$$\alpha(T_r) = b_0 + \frac{b_1}{T_r} + \frac{b_2}{T_r^2} + \frac{b_3}{T_r^3} + \dots \quad (13)$$

with

$$b_j = 0.20268(\lambda^3 - 1) \frac{(\epsilon/kT_c)^{j+1}}{j!} \quad j = 0, 1, 2, \dots \quad (14)$$

Equation 13 is a power series with an infinite number of coefficients but only two unknowns. However, for flexibility, we take empirically the coefficients to be independent. By use of this empiricism, eq 13 can be subjected to any number of constraints. Our evaluation has shown that the first four terms are sufficient to describe the PVT behavior of supercritical fluids. The coefficient b_0 will be zero at high temperature ($T_r \rightarrow \infty$) if the α function should decrease monotonically to zero with temperature, i.e., $b_0 = 0$. If eq 13 will be continuous at the critical point ($T_r \rightarrow 1$), the following constraint also holds:

$$b_1 + b_2 + b_3 = 1 \quad (15)$$

Therefore, Soave's α function is augmented to

$$\alpha(T_r) = \begin{cases} [1 + m(1 - \sqrt{T_r})]^2 & T_r \leq 1 \\ \frac{b_1}{T_r} + \frac{b_2}{T_r^2} + \frac{b_3}{T_r^3} & T_r > 1 \end{cases} \quad (16)$$

Considering eq 15, there are three unknowns (b_1 , b_2 , and b_3), but two of them are independent. Mathias⁵ has recently shown that the RK EoS accurately predicts the

second virial coefficient of substances at the critical point. Then the information at the critical point might be adequate for a semitheoretical α function to describe significantly the second virial coefficient of gases at higher temperatures. To find a solution and avoid anomalies in predicting thermodynamic properties at and near the critical point, we propose the equality of slope and curvature at the critical point for the two parts of eq 16. Therefore, applying eqs 5 and 6 to the supercritical part of eq 16, one can get

$$b_1 = 0.25(12 - 11m + m^2) \quad (17)$$

$$b_2 = 0.5(-6 + 9m - m^2) \quad (18)$$

$$b_3 = 0.25(4 - 7m + m^2) \quad (19)$$

where the parameter m is given by eq 7.

Results and Discussion

The behavior of Soave's α function and its consequences are well documented.⁶ Figure 1 shows the original Soave's temperature dependence as a function of the reduced temperature for methane, ethane, propane, and n -butane. Shown also in Figure 1 is the behavior of the SW α function developed for the supercritical part of Soave's α function. The SW α function decreases monotonically with temperature and becomes zero at very high temperature, while Soave's α function decreases, becomes a minimum at $T_r = (1 + 1/m)^2$, and then increases with temperature. Figure 1 also shows that the two curves coincide at the critical point. However, this is not surprising knowing that both curves have the same slope and curvature at the critical point. In fact, both functions predict the α values with the same quality around the critical point; however, the difference becomes substantial with increasing temperature and also carbon number.

A property that can reflect the accuracy of a temperature dependence for α functions is the second virial coefficient of gases.⁵ The second virial coefficient is explicitly related to the α function as given by eq 11. Figure 2 demonstrates the experimental and predicted

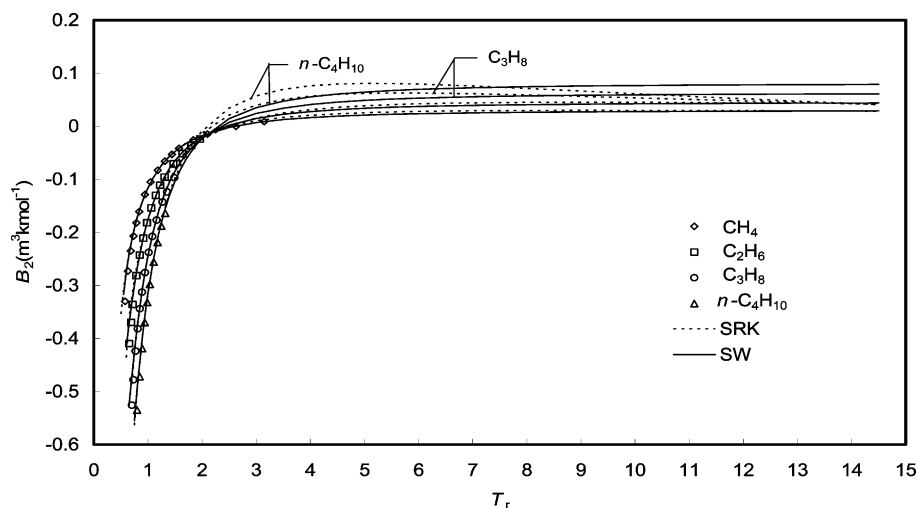


Figure 2. Experimental²⁰ (symbols) and predicted (lines) second virial coefficients for the first four normal alkanes.

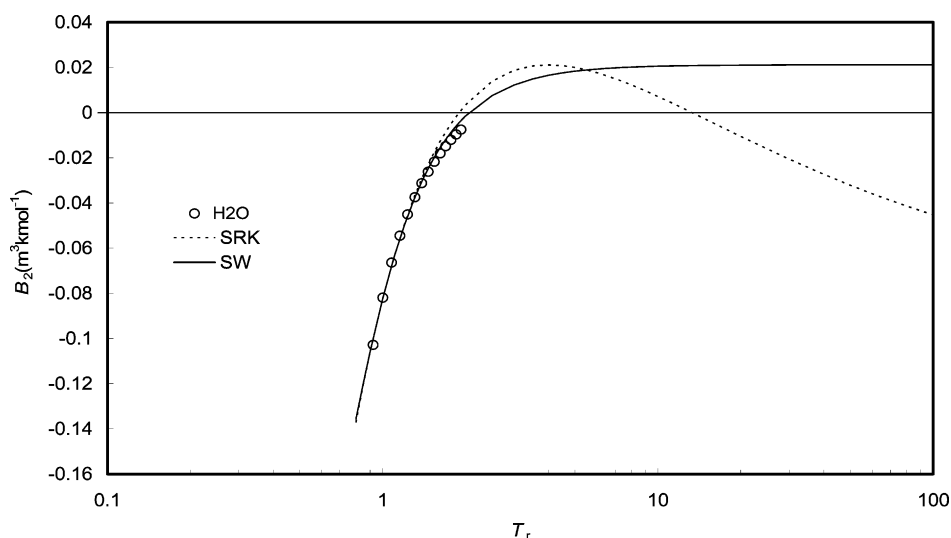


Figure 3. Experimental²⁰ (symbol) and predicted (lines) second virial coefficients for water.

second virial coefficient of methane, ethane, propane, and *n*-butane as a function of the reduced temperature. Both functions predict the experimental data with the same quality. For methane and ethane, the two functions behave similarly at temperatures higher than the experimental data temperature range. However, for propane and *n*-butane, the difference is large at high temperature. Soave's α function predicts maxima for these substances and then decreases with temperature. Strictly speaking, this behavior is not incorrect. However, with a further increase in the temperature, the second virial coefficient predicted by the SRK EoS would change sign. This behavior is best seen for water in Figure 3. As shown in Figure 3, both equations are in good agreement with the experimental data. However, Soave's α function begins to deviate at a reduced temperature of 1.8, while the SW α function follows the experimental data. Also, as clarified by Segura et al.,⁶ one can conclude that Soave's α function predicts two inversion points, two Boyle temperatures, and two critical points that are not consistent with observations.

Figure 4 compares the predicted and experimental second virial coefficients of some refrigerants. Clearly, the agreement is quite good. However, the deviation becomes appreciable at low temperatures. According to our evaluations, the SW α function must not be ex-

tended to reduced temperatures of less than 0.8; otherwise, the prediction of thermodynamic properties gets worse. This behavior can best be seen in Figure 5, where both the SW and Soave's α functions are used to predict the vapor pressure of methane and hydrogen sulfide. Figure 5 depicts the percent deviation defined by

$$\% \text{ Dev} = \frac{\text{cald} - \text{expl}}{\text{expl}}(100) \quad (20)$$

for predicting the vapor pressure of methane and hydrogen sulfide as a function of the reduced temperature. As can be seen, both functions predict the vapor pressure of both substances with the same quality for a T_r range from 0.8 to 1, but the deviation becomes remarkable for the SW α function at lower reduced temperatures.

The temperature at which the second virial coefficient changes sign, the Boyle temperature, is a good indication of the accuracy of EoSs in predicting the second virial coefficient of substances. In Table 1, experimental and predicted Boyle temperatures of certain gases using the SW and Soave's α functions are compared. Given also in Table 1 are the predictions of the Boyle temperature from a modified Redlich-Kwong (RK-TCC) by Twu et al.,¹⁵ the PR EoS, and a modified Peng-Robinson (PR-GGPR) by Gasem et al.⁸ Clearly, the SW

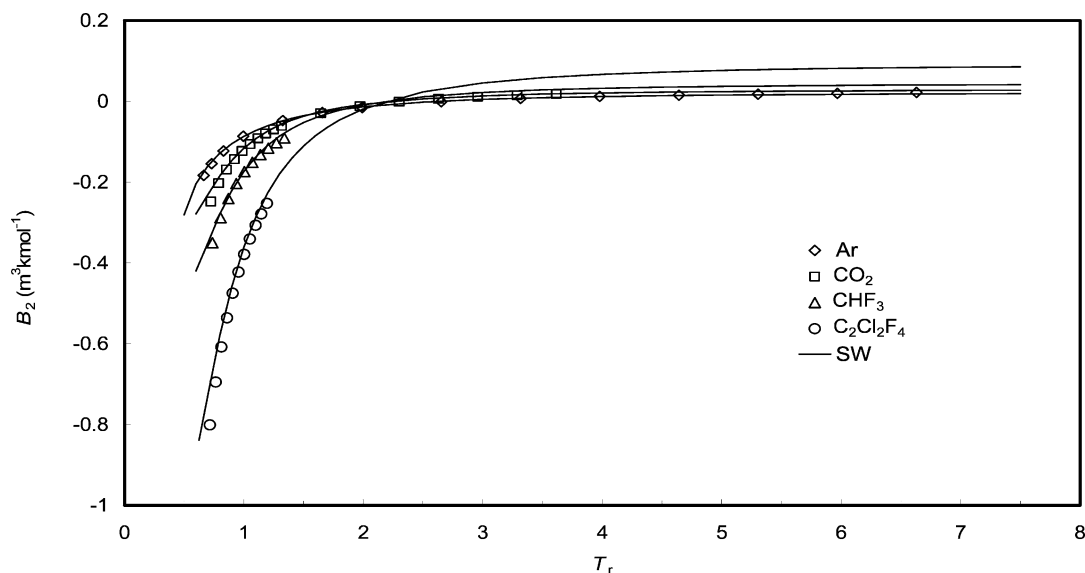


Figure 4. Experimental²⁰ (symbols) and predicted (lines) second virial coefficients for some refrigerants.

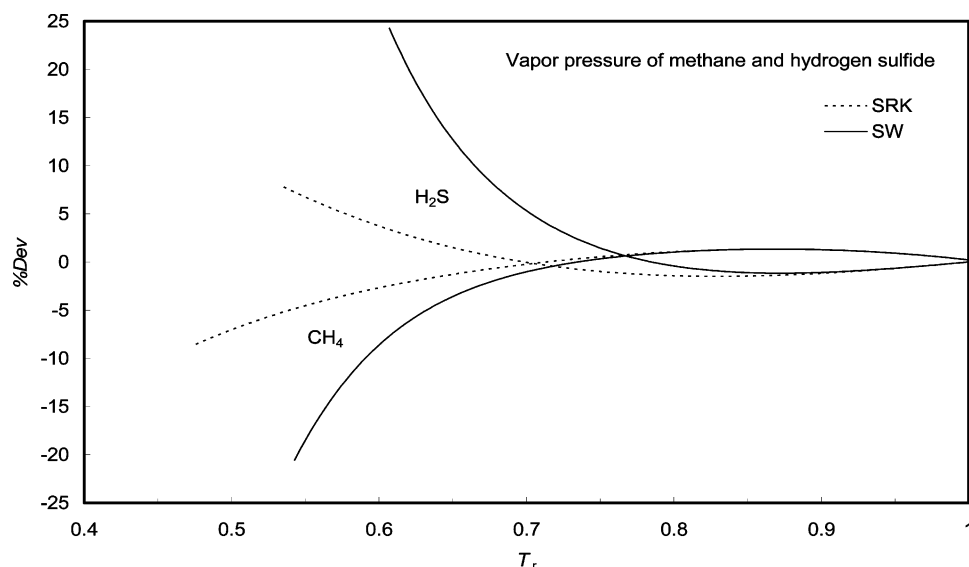


Figure 5. Percent deviation between the predicted and experimental²¹ vapor pressures of methane and hydrogen sulfide.

Table 1. Experimental and Predicted Boyle Temperature (T_B/T_c) for Certain Fluids

compd	experiment	SW	SRK	RK-TCC	PR	PR-GGPR
Ar ²²	2.711	2.638	2.538	2.475	3.060	2.947
Kr ²²	2.714	2.624	2.516	2.468	3.025	2.920
Xe ²²	2.673	2.638	2.538	2.475	3.060	2.947
CH ₄ ²³	2.670	2.612	2.497	2.463	2.995	2.896
CO ₂ ²³	2.343	2.236	2.048	2.257	2.324	2.341
N ₂ ²⁴	2.577	2.562	2.422	2.438	2.877	2.803
H ₂ O ²³	2.35	2.067	1.902	2.145	2.123	2.160
Ne ²²	2.867	2.666	2.584	2.488	3.135	3.006
He ²⁵	4.33	3.503	8.402	2.841	25.634	—
% AAD ^a		4.21	9.91	7.99	10.31	7.10

^a Helium is not included.

α function is in best agreement with the experimental Boyle temperature for the given substances. The percent average absolute deviation defined by

$$\% \text{AAD} = (100/n) \sum_j^n |\text{cald}_j - \text{expl}_j| / \text{expl}_j \quad (21)$$

was found to be 4.21% for the SW α function, 9.91% for Soave, and 7.99%, 10.31%, and 7.10% for RK-TCC, PR,

and PR-GGPR, respectively. It is also worth noting that the SW α function predicts the Boyle temperature of helium, with a significant quantum effect, remarkably better than the other EoSs.

Figure 6 illustrates the second virial coefficient of hydrogen as a function of the reduced temperature. At low temperature, hydrogen shows a quantum effect and is not classified among normal fluids where the realm of the SRK EoS is. However, it is known that the SRK EoS predicts the phase equilibria of mixtures containing hydrogen. This can best be understood from Figure 6. Soave's α function predicts the experimental hydrogen second virial coefficients accurately. However, the prediction of the SW α function is evidently better. For comparison, the predictions from RK-TCC, PR, and PR-GGPR EoSs are also given. The SW is clearly superior, while the PR EoS is inferior.

Figure 7 compares the experimental and predicted isobaric heat capacity of propane along the critical isotherm where the SW α function is connected to Soave's α function. When it is known that the first and second derivatives of α functions are used in calculating

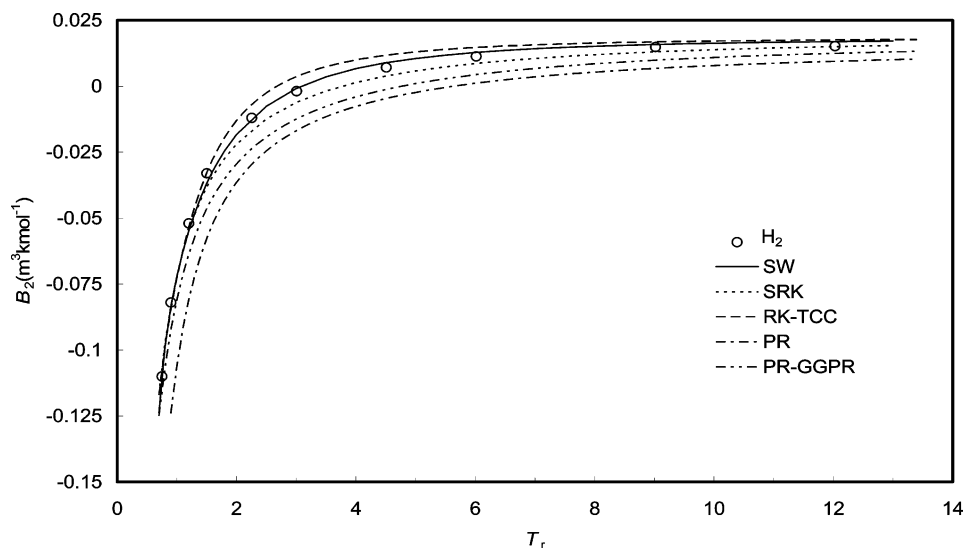


Figure 6. Experimental²⁰ (symbol) and predicted (lines) second virial coefficients for hydrogen.

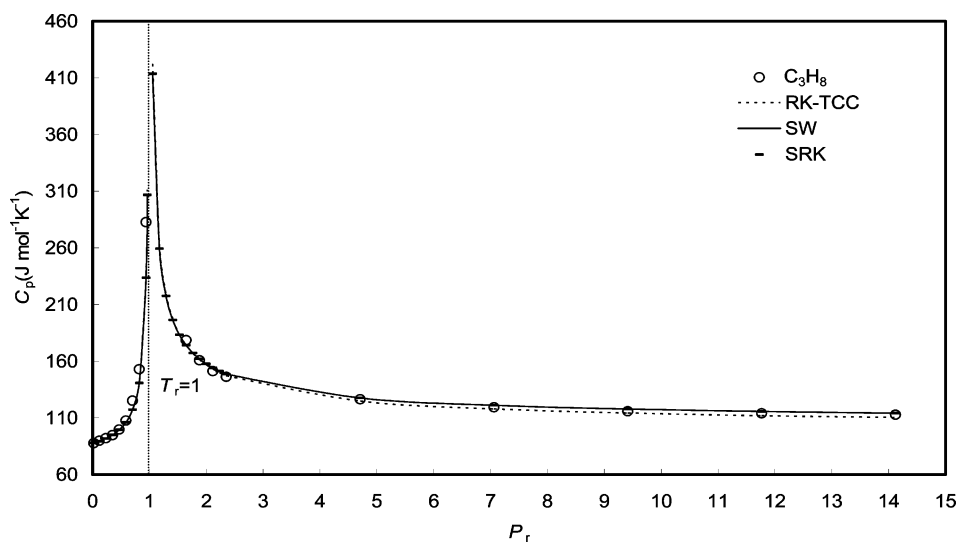


Figure 7. Experimental²⁶ (circle) and predicted isobaric heat capacities for propane along the critical isotherm.

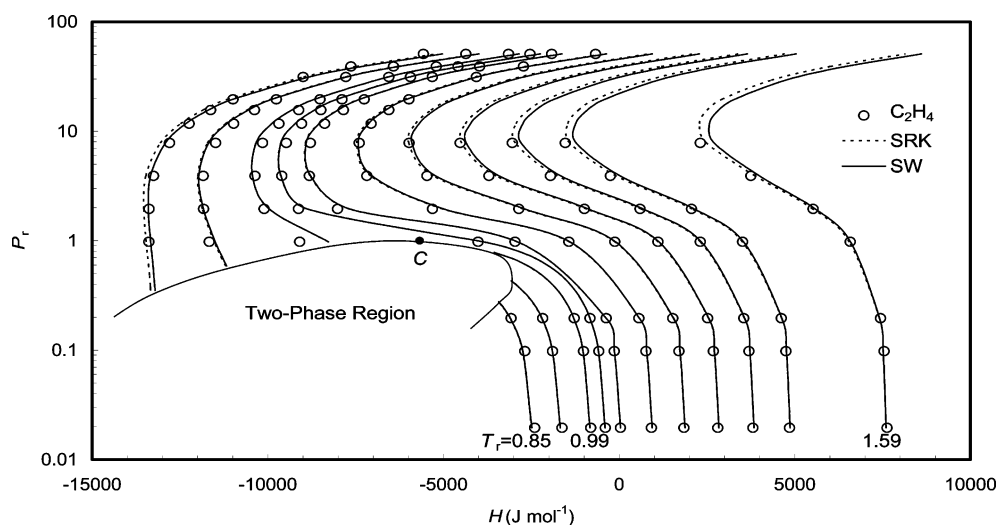


Figure 8. IUPAC-recommended²⁷ (circle) and predicted enthalpies of ethylene for single-phase region.

isobaric heat capacities, Figure 7 elucidates that connecting the SW and Soave's α functions at the critical point does not pose anomalous behavior in predicting thermodynamic properties. The predictions from the RK-TCC EoS are also included. A further example is

shown in Figure 8, where the enthalpies of ethylene as predicted by the SW and Soave's α functions are compared for wide ranges of temperature and pressure with the recommended values of IUPAC tables for the single-phase region. The agreement with the IUPAC

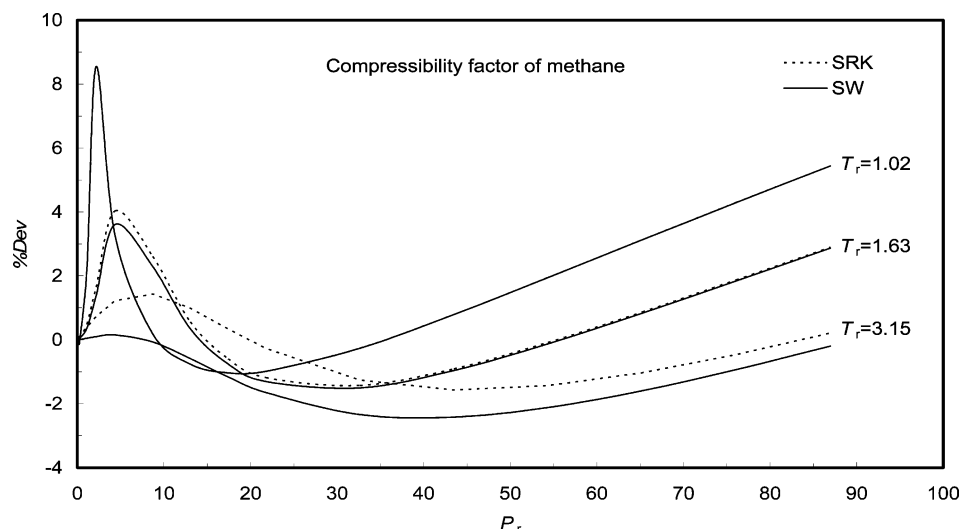


Figure 9. Percent deviation between the predicted and IUPAC-recommended compressibility factors for methane.²⁸

Table 2. Accuracy (% AAD) of the EoSs for Predicting the Isobaric Heat Capacities of Certain Gases

compound	<i>n</i>	<i>T_r</i> range	<i>P_r</i> range	SW	SRK	RK-TCC	PR	PR-GGPR
CH ₄ ²⁸	130	1.02–3.15	0.02–86.98	1.74	1.62	3.83	1.9	2.20
C ₂ H ₆ ²⁶	66	1.02–1.64	0.02–10.26	1.61	1.29	2.07	1.30	1.29
C ₃ H ₈ ²⁶	68	1.00–1.62	0.02–14.12	1.44	1.06	1.79	1.00	1.04
<i>i</i> -C ₄ H ₁₀ ²⁶	40	1.04–1.34	0.03–4.40	0.80	0.83	0.73	1.01	1.05
N ₂ ²⁴	180	1.03–8.72	0.03–117.71	1.53	1.36	2.27	1.36	1.91
F ₂ ²⁹	110	1.01–2.08	0.02–3.84	4.04	4.00	4.23	4.04	4.03
NH ₃ ²⁶	100	1.04–1.43	0.01–9.70	7.14	5.96	8.34	5.56	5.35
average				2.73	2.42	3.59	2.43	2.60

Table 3. Accuracy (% AAD) of the EoSs for Predicting the Compressibility Factors of Certain Gases

compound	<i>n</i>	<i>T_r</i> range	<i>P_r</i> range	SW	SRK	RK-TCC	PR	PR-GGPR
CH ₄ ²⁸	154	1.02–3.15	0.21–86.98	1.36	1.41	1.62	6.29	6.09
C ₂ H ₆ ²⁶	72	1.02–1.64	0.02–10.26	2.30	2.57	2.75	2.69	2.67
C ₃ H ₈ ²⁶	79	1.00–1.62	0.02–14.12	2.90	3.10	3.12	2.82	2.84
<i>n</i> -C ₄ H ₁₀ ²⁶	29	1.05–1.20	0.26–17.91	4.54	4.61	4.72	4.67	4.69
Ar ²²	116	1.03–8.62	0.02–20.42	0.84	0.63	0.89	2.50	2.22
N ₂ ²⁴	95	1.03–8.72	0.03–117.7	1.59	1.39	1.53	4.58	4.47
O ₂ ³⁰	63	1.04–1.94	0.02–15.86	1.15	1.26	1.67	3.69	3.57
CO ₂ ³¹	104	1.02–3.62	0.01–13.56	2.14	2.95	2.13	1.28	1.29
C ₃ H ₆ ³²	100	1.01–1.58	0.17–86.96	2.27	2.36	2.44	4.67	4.68
NH ₃ ²⁶	93	1.04–1.43	0.01–9.69	10.91	11.13	11.02	6.34	6.27
average				2.78	2.92	2.96	4.05	3.96

values is quite good for both α functions. In Table 2, the accuracy of the SW and Soave's α functions in terms of % AAD for predicting the isobaric heat capacity of certain gases is presented. The predicted values by the other EoSs are also included for comparison. The SRK EoS is in better agreement with experimental data and recommended values of IUPAC tables than the other EoSs. However, the SW predicts the isobaric heat capacities considerably better than the RK-TCC EoS. It is also interesting to note that both the SRK and PR EoSs are superior than their modifications in predicting the isobaric heat capacities. Evidently, the Soave-type α function is more consistent with the SRK and PR EoSs in predicting isobaric heat capacities.

In Table 3, the predicted compressibility factors of certain gases from the EoSs are compared with experimental data and recommended values of IUPAC tables. As can be seen, the SW is in best agreement with experimental data and IUPAC values except for nitrogen. As indicated also in Table 3, the RK family of EoSs are generally in better agreement with the IUPAC recommended values than the PR family. Figure 9 demonstrates a deviation plot for predicting the meth-

ane compressibility factor as a function of the reduced pressure, with the reduced temperature as a third parameter. Figure 9 reveals that near the critical point, i.e., $T_r = 1.02$, both functions deviate similarly from IUPAC values; however, with an increase in the reduced temperature from 1.02 to 3.15, the deviations become remarkable at low to moderate pressure. As is also shown in Figure 9, with an increase in the pressure, the deviations become similar. This behavior attributes to the fact that at high pressure, in general, the repulsive terms of the EoSs dominate and weaken the impact of the attractive terms and, consequently, the α function.

Table 4 presents the accuracy of the EoSs in predicting the fugacity of five substances for wide ranges of temperature and pressure. As Flöter et al.¹⁶ showed, the accuracy of the PR EoS in the high-temperature, high-pressure phase equilibria of binary asymmetric mixtures containing methane to a large extent depends on the accuracy of the PR EoS in predicting the fugacity of methane. Table 4 indicates that the SW α function considerably describes the fugacity of the components, especially methane, better than Soave's α function and the other EoSs. Then, the SW α function might

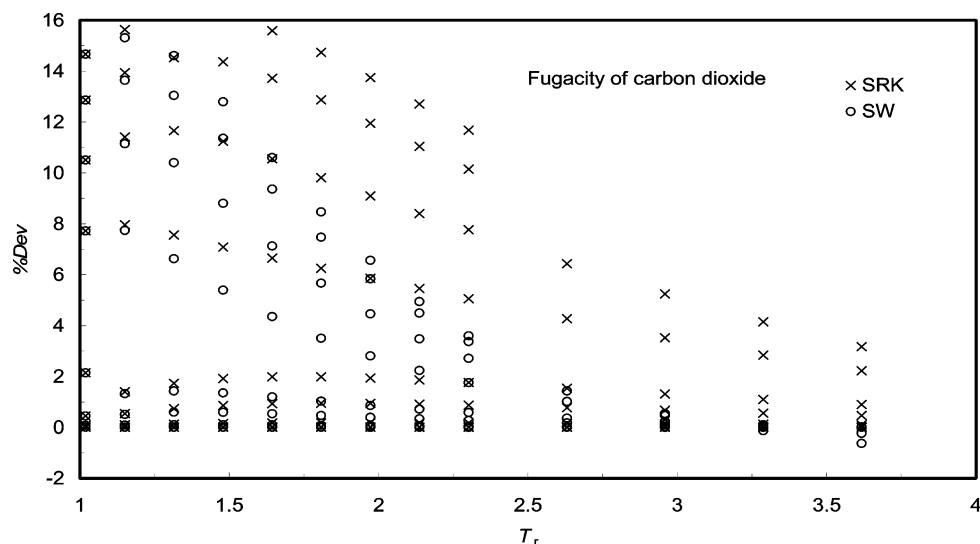


Figure 10. Percent deviation between the predicted and IUPAC-recommended fugacities of carbon dioxide.³¹

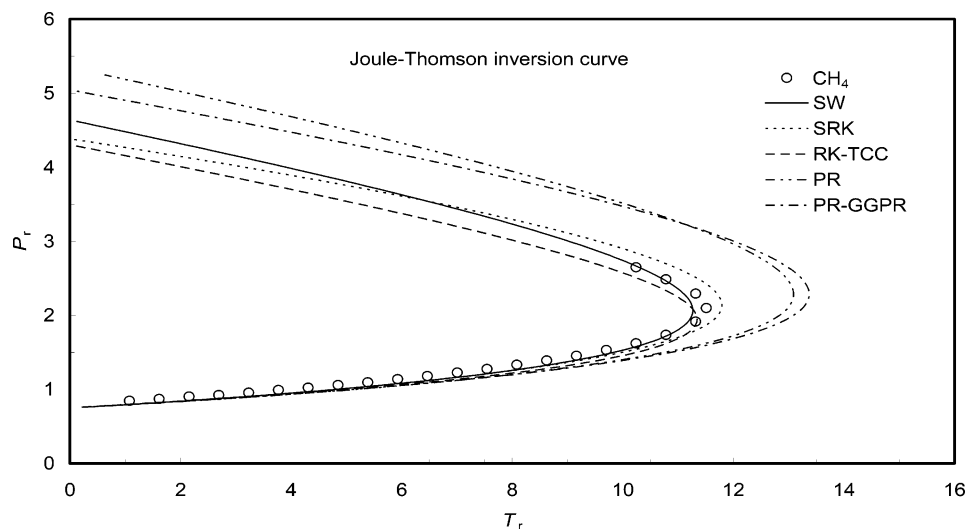


Figure 11. Experimental³³ (circle) and predicted Joule–Thomson inversion curves for methane.

Table 4. Accuracy (% AAD) of the EoSs for Predicting the Fugacities of Certain Fluids

compound	<i>n</i>	<i>T_r</i> range	<i>P_r</i> range	SW	SRK	RK-TCC	PR	PR-GGPR
CH ₄ ²⁸	176	1.02–3.15	0.21–86.98	2.77	3.66	5.64	13.55	12.81
N ₂ ²⁴	155	1.03–7.92	0.29–29.43	2.04	1.63	2.41	8.51	7.93
CO ₂ ³¹	122	1.02–3.62	0.001–13.56	2.47	3.79	2.43	0.57	0.56
C ₂ H ₄ ²⁷	66	1.01–1.59	0.02–5.95	3.71	3.81	4.20	7.20	7.20
C ₃ H ₆ ³²	56	1.00–1.58	0.02–86.96	5.69	5.87	6.12	9.81	9.86
average				2.90	3.37	3.97	8.34	7.96

improve the SRK EoS in high-temperature, high-pressure fluid phase equilibria of asymmetric mixtures. Figure 10 shows a deviation plot for the fugacity of carbon dioxide as a function of the reduced temperature. Clearly, the SW α function is more accurate than Soave's α function for predicting the fugacity of carbon dioxide. As is also shown in Figure 10, the deviations are larger at lower temperature than at higher temperature.

Finally, Figure 11 shows the Joule–Thomson inversion curve for methane. Only the SW describes the entire curve significantly. The SW predicts not only the lower branch but also the upper branch. The lower branch is also predicted by the RK-TCC and SRK equations. The maximum inversion point is only predicted by the SW and RK-TCC, however.

Conclusion

On the basis of the SW potential, an equation to describe the supercritical behavior of Soave's α function has been derived. The parameters of the SW α function have been obtained by subjecting the model to the slope and curvature of the original Soave's α function. No adjustable parameters were used; however, the agreement with the experimental second virial coefficient data for the SW α function has been satisfactory for a reduced temperature range from 0.8 and higher. In the expense of predicting the worst isobaric heat capacity, the SW α function predicts the compressibility factor and fugacity of substances better than Soave's α function. As a consequence, for calculation of the volumetric properties and fluid-phase equilibria of mixtures, the

proposed equation can be used in conjunction with the SRK EoS to predict the supercritical part of the α function while the original Soave's α function is still valid for the critical and supercritical temperatures.

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