

Generalized Vapor Pressure Prediction Consistent with Cubic Equations of State

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Introduction

Equations of state may be used to calculate pure component vapor-liquid equilibrium properties such as vapor pressure, heat of vaporization, liquid density, and vapor density. The standard approach requires coupling the EOS with a phase equilibrium criterion such as free energy, chemical potential, or fugacity. The resulting equations are nonlinear and must be solved by numerical methods.

An alternative approach is applicable to cubic EOS such as the commonly used Soave-Redlich-Kwong and Peng-Robinson equations. Equilibrium properties may be explicitly expressed as power series in reduced temperature or related functions. These results are more convenient than numerical calculations, but are subject to truncation error in many practical situations.

Results from such a power series method for the SRK equation were used to generate generalized dimensionless vapor pressure equations which were extensions of the commonly used Antoine equation but valid over wider temperature ranges. The substance-specific adjustable constants of the vapor pressure equations were expressed as functions of the acentric factor of the substance and its critical temperature and pressure. The deviations between these results and the exact vapor pressure predictions from the SRK equation were quantitatively characterized.

VLE from Cubic Equations of State

Cubic equations of state of the Van der Waals type are widely used in chemical engineering practice because they provide a reasonable balance between accuracy and simplicity. Two common examples are the Soave-Redlich-Kwong [1] and Peng-Robinson [2] equations, shown below as Eqs. (1) and (2),

$$P = \frac{RT}{V - b_{SRK}} - \frac{a_{SRK}(T)}{V(V + b_{SRK})} \quad (1)$$

$$P = \frac{RT}{V - b_{PR}} - \frac{a_{PR}(T)}{V(V + b_{PR}) + b_{PR}(V - b_{PR})} \quad (2)$$

In these equations, the attractive function $a_{EQ}(T)$ has the form

$$a_{EQ}(T) = a_{c,EQ} [1 + f_{EQ}(\omega)(1 - T_r^{1/2})]^2 \quad (3)$$

with the critical value of

$$a_{c,EQ} = \frac{a_{0,EQ} R^2 T_c^2}{P_c} \quad (4)$$

and the acentric factor functions given by

$$f_{SRK}(\omega) = 0.480 + 1.574\omega - 0.176\omega^2 \quad (5)$$

$$f_{PR}(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (6)$$

The occupied volume parameter b is given by

$$b_{EQ} = \frac{b_{0,EQ} R T_c}{P_c} \quad (7)$$

Values of the dimensionless numerical constants in Eqs. (4) and (7) are $a_{0,SRK} = 0.42748$, $a_{0,PR} = 0.45724$, $b_{0,SRK} = 0.08664$, and $b_{0,PR} = 0.07780$.

Like many equations of state, SRK and PR may be used to calculate vapor pressure and other pure component vapor-liquid equilibrium properties. Doing this requires coupling the EOS with a phase equilibrium criterion such as free energy, chemical potential, or fugacity. Eqs. (8) and (9) give expressions for the pure component fugacity coefficient for SRK and PR.

$$\ln \phi_{SRK} = z - 1 - \ln z - \ln(1-h) - \frac{a_{SRK}}{b_{SRK} RT} \ln(1+h) \quad (8)$$

$$\ln \phi_{PR} = z - 1 - \ln z - \ln(1-h) - \frac{a_{PR}}{2\sqrt{2}b_{PR} RT} \ln \frac{1+h(1+\sqrt{2})}{1+h(1-\sqrt{2})} \quad (9)$$

$$z = \frac{PV}{RT} \quad (10)$$

$$h = \frac{b_{EQ}}{V} \quad (11)$$

When an equilibrium state exists, Eq. (1) gives three real roots for volume from SRK. The smallest and largest of these are liquid and vapor volumes, respectively. The fugacity coefficients calculated by Eq. (8) will be equal when the liquid volume is substituted and when the vapor volume is substituted. For PR, Eqs. (2) and (9) are used. A numerical algorithm is required to solve either of these sets of nonlinear equations.

Power Series Methods for Cubic Equation VLE

A formal procedure [3] is available to express results for phase densities and vapor pressure of coexisting liquid and vapor phases as analytic power series in temperature. The approach begins by writing reduced deviation variables for phase densities ($\Delta\rho^L$ and $\Delta\rho^V$) and temperature (ΔT) about the critical point. These variables are defined as

$$\Delta M = M_r - 1 = \frac{M - M_c}{M_c} \quad (12)$$

with M representing either ρ^L , ρ^V , or T. The resulting formal power series are

$$P_r = \sum_{j=0}^{\infty} A_j (\Delta T)^j \quad (13)$$

$$\Delta \rho^L = \sum_{i=1}^{\infty} B_i (-\Delta T)^{i/2} \quad (14)$$

$$\Delta \rho^V = \sum_{i=1}^{\infty} (-1)^i B_i (-\Delta T)^{i/2} \quad (15)$$

After equilibrium constraints are applied to these series, the coefficients A_j and B_i are observed to be functions of the acentric factor function $f_{EQ}(\omega)$ which depend upon the cubic EOS being applied. They are substance-dependent since they contain the acentric factor function. For SRK and PR, A_j is given by a polynomial of degree j in the acentric factor function, B_i is given by a polynomial of degree $(i-1)$ in the acentric factor function for even i , and by a similar polynomial multiplied by the square root of $(1 + f_{EQ}(\omega))$ for odd i . Expressions for these polynomials have been tabulated. [4,5]

The utility of this method stems from the convenience of direct computation of coexisting phase properties without need for auxiliary equilibrium criteria such as fugacities. The weaknesses of the method arise from being based upon a series expansion about the critical point. In practice, the infinite series given by Eqs. (13) to (15) must be truncated. Few terms are required near the critical point, but this is the situation where cubic EOS are least accurate. At moderately high or moderate temperatures, where the equations have reasonable accuracy, many series terms are needed to prevent truncation error. The magnitude of truncation error also depends upon the property (phase density or vapor pressure) and varies with acentric factor. In general, truncation errors are largest for vapor density and smallest for liquid density, they are larger for the PR equation as compared to SRK, and they increase with increasing acentric factor.

Generalized Antoine Vapor Pressure Functions Derived from Power Series

In previous work, a generalized form of the Antoine vapor pressure equation was developed. In the traditional Antoine equation, dimensional constants are used to fit vapor pressure data over a temperature range.

$$\ln P = A - \frac{B}{T + C} \quad (16)$$

This was adapted by writing the Antoine equation in reduced variables as Eq. (17) where the constants are expressed as functions of the acentric factor.

$$\ln P_r = A^* - \frac{B^*}{T_r + C^*} \quad (17)$$

Results for the functions A^* , B^* , and C^* for the SRK equation are available for reduced temperatures in the range $0.6 < T_r < 1.0$, and for the PR equation in the range $0.7 < T_r < 1.0$. [6] A sample of typical results is shown in Table 1. As is the case with the traditional Antoine equation, the range of accuracy is limited -- in this example to reduced temperatures between 0.70 and 0.84. Figure 1 illustrates the accuracy of the method. Each curve in Figure 1 represents a different acentric factor. Within the specified temperature range ($0.70 < T_r < 0.84$) the vapor pressures predicted by Eq. (17) match the exact SRK vapor pressures to within less than 0.1 percent deviation for all acentric factors between -0.12 and +0.72.

Table 1. Antoine Constant Functions for the SRK Equation for $0.70 < T_r < 0.84$.

$$A^* = 4.4401 + 2.2128f_{\text{SRK}}(\omega) - 0.53518f_{\text{SRK}}(\omega)^2 + 0.17368f_{\text{SRK}}(\omega)^3 - 0.018512f_{\text{SRK}}(\omega)^4$$

$$B^* = 5.0075 + 1.2494f_{\text{SRK}}(\omega) - 0.78155f_{\text{SRK}}(\omega)^2 + 0.32010f_{\text{SRK}}(\omega)^3 - 0.047601f_{\text{SRK}}(\omega)^4$$

$$C^* = 0.124652 - 0.273702f_{\text{SRK}}(\omega) + 0.0750076f_{\text{SRK}}(\omega)^2 - 0.0137818f_{\text{SRK}}(\omega)^3 + 0.00145038f_{\text{SRK}}(\omega)^4$$

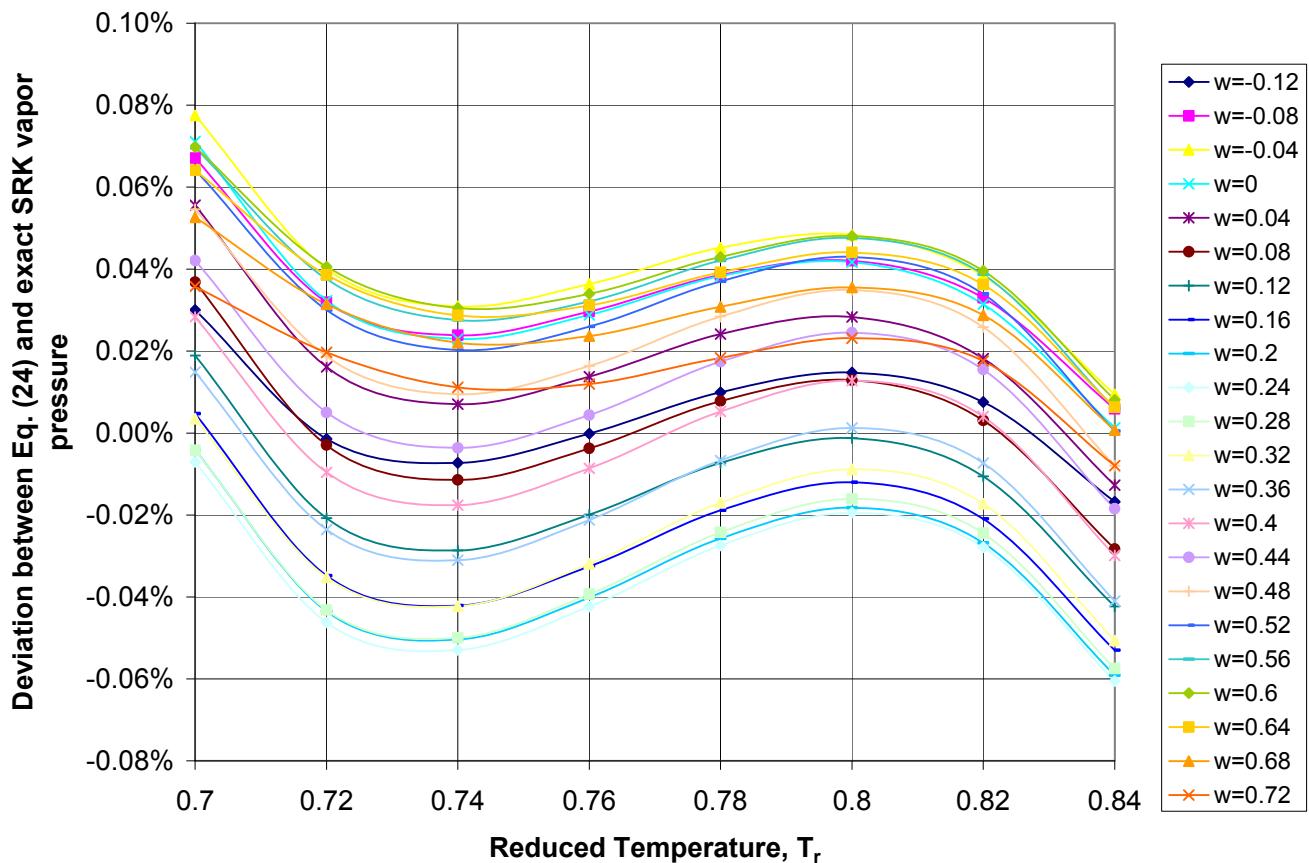


Figure 1. Percentage Deviation between Vapor Pressure Predicted by Generalized Antoine Equation, Eq. (17), and Exact SRK Vapor Pressure for Various Acentric Factors.

In the current work, the method was adapted and applied to generalized versions of extended forms of the Antoine equation, given by Eqs. (18) and (19).

$$\ln P_r = A^* - \frac{B^*}{T_r} + K_1^* \ln T_r \quad (18)$$

$$\ln P_r = A^* - \frac{B^*}{T_r + C^*} + K_4^* T_r + K_5^* \ln T_r \quad (19)$$

Analogous to Eq. (17), the constants in Eqs. (18) and (19) were polynomials of the acentric factor function $f_{\text{SRK}}(\omega)$. Some examples of these functions are shown in Tables 2 and 3.

Like Eq. (17), the generalized extended Antoine equation given by Eq. (18) was capable of estimating vapor pressures within less than 0.1 percent deviation from the exact SRK values for the reduced temperature range $0.6 < T_r < 1.0$. Also like Eq. (17), three distinct sets of Antoine constant functions were needed to span this temperature range. One advantage of Eq. (18) was that the Antoine constant functions were cubic polynomials in the acentric factor function $f_{\text{SRK}}(\omega)$, whereas Eq. (17) required quartic (4th degree) polynomials to achieve the same accuracy of prediction.

Table 2. Extended Antoine Constant Functions in Eq. (18) for the SRK Equation for the Temperature Range $0.60 < T_r < 0.72$.

$$\begin{aligned} A^* &= 2.8278 + 4.8255 f_{\text{SRK}}(\omega) + 2.7682 f_{\text{SRK}}(\omega)^2 - 0.057280 f_{\text{SRK}}(\omega)^3 \\ B^* &= 2.8422 + 4.8991 f_{\text{SRK}}(\omega) + 2.8244 f_{\text{SRK}}(\omega)^2 - 0.069460 f_{\text{SRK}}(\omega)^3 \\ K_1^* &= 1.1068 - 2.2926 f_{\text{SRK}}(\omega) - 3.2566 f_{\text{SRK}}(\omega)^2 + 0.13569 f_{\text{SRK}}(\omega)^3 \end{aligned}$$

Table 3. Extended Antoine Constant Functions in Eq. (19) for the SRK Equation for the Temperature Range $0.60 < T_r < 1.0$.

$$\begin{aligned} A^* &= 2.5713 + 3.8253 f_{\text{SRK}}(\omega) + 0.56359 f_{\text{SRK}}(\omega)^2 + 0.42434 f_{\text{SRK}}(\omega)^3 - 0.011805 f_{\text{SRK}}(\omega)^4 \\ B^* &= 4.2778 + 6.9822 f_{\text{SRK}}(\omega) + 6.8127 f_{\text{SRK}}(\omega)^2 - 0.57592 f_{\text{SRK}}(\omega)^3 - 0.027427 f_{\text{SRK}}(\omega)^4 \\ C^* &= 0.031642 + 0.00022474 f_{\text{SRK}}(\omega) - 0.00095525 f_{\text{SRK}}(\omega)^2 + 0.00074762 f_{\text{SRK}}(\omega)^3 \\ &\quad - 0.00017628 f_{\text{SRK}}(\omega)^4 \\ K_4^* &= 1.5758 + 2.9403 f_{\text{SRK}}(\omega) + 6.0484 f_{\text{SRK}}(\omega)^2 - 0.98555 f_{\text{SRK}}(\omega)^3 - 0.014798 f_{\text{SRK}}(\omega)^4 \\ K_5^* &= -1.5345 - 6.4179 f_{\text{SRK}}(\omega) - 12.447 f_{\text{SRK}}(\omega)^2 + 1.5234 f_{\text{SRK}}(\omega)^3 + 0.036455 f_{\text{SRK}}(\omega)^4 \end{aligned}$$

Eq. (19) was more complex than Eqs. (17) and (18) because it contained five Antoine constant functions instead of three. The advantage of Eq. (19) was that a single set of Antoine constant functions, shown in Table 3, was able to estimate SRK vapor pressures within the specified deviation for the entire reduced temperature range $0.60 < T_r < 1.0$, as Figure 2 verifies.

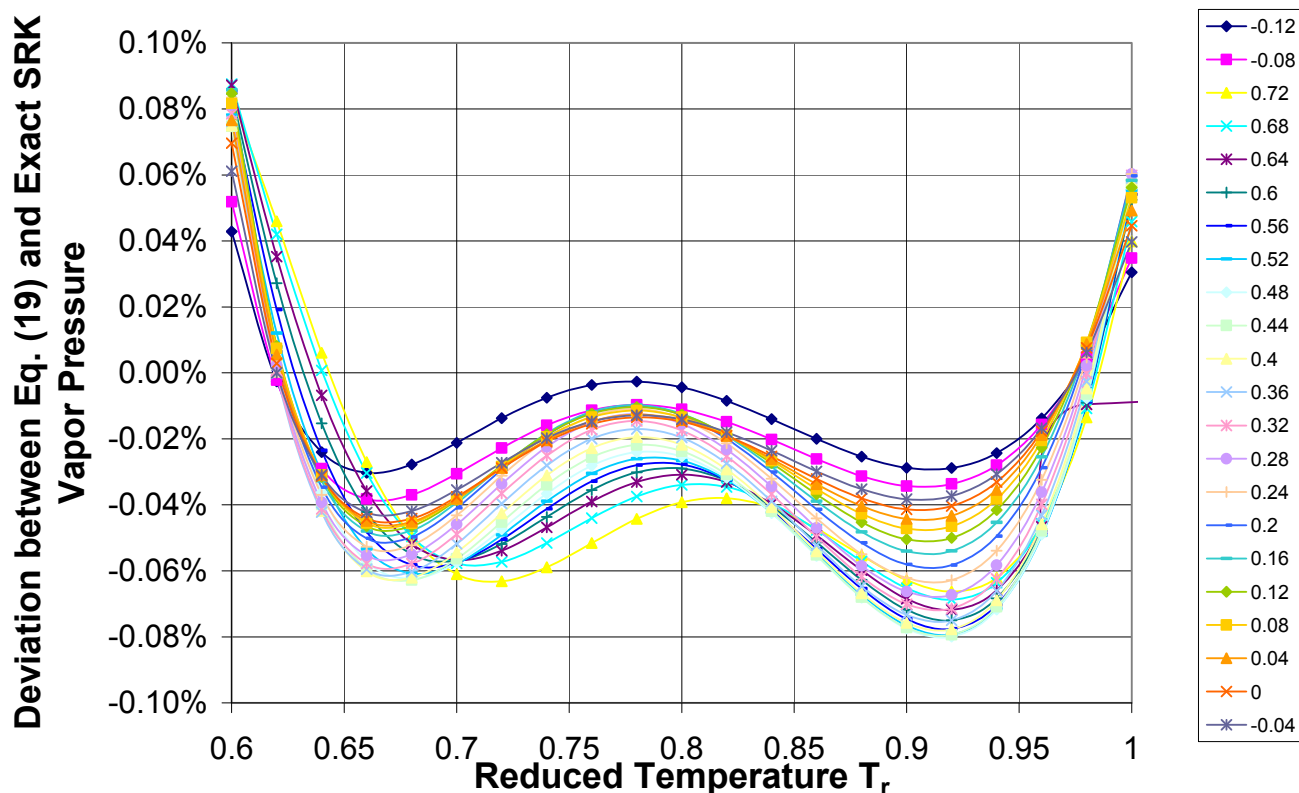


Figure 2. Percentage Deviation between Vapor Pressure Predicted by Generalized Extended Antoine Equation, Eq. (19), and Exact SRK Vapor Pressure for Various Acentric Factors.

Work continues on adapting these methods to other extended versions of the Antoine equation, especially those commonly used in process simulation software, to other cubic EOS such as PR, and to additional temperature ranges.

Conclusions

Results for a generalized dimensionless form of two versions of an extended Antoine equation were presented. These were shown to reproduce the vapor pressure predictions of the SRK cubic equation of state to within 0.1 percent deviation over the temperature range $0.60 < T_r < 1.0$ for all acentric factors between -0.12 and +0.72.

Acknowledgements

This material is based upon work supported by the Michigan Space Grant Consortium and by the Brookstra Faculty Development Fund. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of these institutions.

Nomenclature

A	Constant in Eq. (16), Antoine vapor pressure equation
A [*]	Function of acentric factor in Eqs. (17) to (19), generalized Antoine vapor pressure equations
A _j	temperature coefficients in Eq. (13) for reduced pressure
a _{EQ} (T)	energy parameter in attractive term
a _{c,EQ}	energy parameter in attractive term at the critical point
a _{0,EQ}	dimensionless numerical coefficient of energy parameter
B	Constant in Eq. (16), Antoine vapor pressure equation
B [*]	Function of acentric factor in Eqs. (17) to (19), generalized Antoine vapor pressure equations
B _i	temperature coefficients in Eqs. (14) and (15) for reduced density deviation variables
b _{EQ}	excluded volume parameter in equation of state
b _{0,EQ}	dimensionless numerical coefficient of excluded volume parameter
C	Constant in Eq. (16), Antoine vapor pressure equation
C [*]	Function of acentric factor in Eqs. (17) and (19), generalized Antoine vapor pressure equations
f _{EQ} (ω)	quadratic function of acentric factor
h	ratio of excluded volume parameter to molar volume
K ₁ [*]	Function of acentric factor in Eq. (18), generalized Antoine vapor pressure equation
K ₄ [*]	Function of acentric factor in Eq. (19), generalized Antoine vapor pressure equation
K ₅ [*]	Function of acentric factor in Eq. (19), generalized Antoine vapor pressure equation
M	general thermodynamic state property (T, ρ ^L or ρ ^V) in Eq. (12)
P	absolute pressure
R	gas constant
T	absolute temperature
V	molar volume
z	compressibility

Greek letters

ΔM	reduced deviation variable of state property M (T, ρ ^L or ρ ^V) defined by M _r – 1
ρ	molar density
φ _{EQ}	fugacity coefficient for equation of state
ω	acentric factor

Subscripts

c	critical (temperature, pressure, or molar density)
EQ	parameter or coefficient applying to equation of state EQ (SRK or PR)
r	reduced (temperature, pressure, or molar density)

Superscripts

L	liquid (molar density or molar volume)
V	vapor (molar density or molar volume)

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