

A Review of the Equations of State and their Applicability in Phase Equilibrium Modeling

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Abstract—This short paper reviews the equations of state and their application to phase equilibrium modeling. The strengths, weaknesses and applicability of these equations will be assessed. Our intention is to test the applicability of the Peng Robinson equation of state in the computation of thermodynamic interactions of volatile organic compounds and biodiesel. Thermodynamic models are very useful in phase equilibrium prediction as measurements are costly and time consuming.

Keywords—Activity coefficients, equations of state, modeling, phase equilibrium.

I. INTRODUCTION

A. Development of Equation of States

IN 1662, Robert Boyle found that the volume of a gas was inversely proportional to its pressure as shown in (1).

$$pV = \text{constant} \quad (1)$$

Charles (1787) postulated that the volume of a gas was proportional to its temperature at isobaric conditions. In 1801, Dalton (1801) introduced the concept of partial pressures. Gay-Lussac (1802) defined the universal gas constant “R”. Van der Waals (1873)’s quantitative approach proposed the continuity of gases and liquids and provided the most important contribution to EOS development. In 1875 Gibbs made an important contribution to thermodynamics. In 1927, Ursell (1927) proposed a series solution (polynomial functional form) for the EOS known as the virial EOS (2).

$$P = 1 + \frac{b}{V} + \frac{c}{V^2} + \frac{d}{V^3} + \dots \quad (2)$$

In 1949, Redlich & Kwong introduced a temperature dependency to the attraction parameter “a” of the vdW EOS. Pitzer (1955) introduced the “acentric factor” to quantify for

the non-sphericity of molecules and related it to vapor pressure data. In 1972, Soave modified the Redlich & Kwong EOS by introducing Pitzer’s acentric factor. Peng and Robinson (1976) proposed their EOS applicable to natural gas systems [1].

B. Definition of Equation State

An Equation of State (EOS) is a semi-empirical functional relationship between pressure, volume and temperature of a pure substance. It is a thermodynamic equation describing the state of matter under a given set of physical conditions. Most EOSs are semi-empirical and are generally developed for pure substances. Their application to mixtures requires an additional variable (composition) and hence an appropriate mixing rule. The functional form of an EOS can be expressed as in (3).

$$f(P, V, T, a_k, k = 1, n_p) = 0 \quad (3)$$

A_k and n_p are the parameters and categories of the equations of state. n_p indicates the complexity of the EOS and the more complex is the equation, the more accurate it is. Currently, there is no single equation of state that accurately predicts the properties of all substances under all conditions [2]. Many cubic EOSs contain the original van der Waals

$$\frac{RT}{(V - b)^2}$$

repulsive term

The Peng Robinson and Soave-Redlich-Kwong equations of state are the most applicable in the petroleum industry [3]. The EOSs were developed to predict volumetric, thermophysical and vapour-liquid equilibrium data [3].

The main purpose for the development of the EOS approach was for generating of data which included volumetric, thermo physical data, and to help perform vapor/liquid equilibrium calculations. [3]

Equations of state can be applied over wide range of temperature and pressure as well as to mixtures of diverse components, from light gases to heavy liquids. They can also be applied to supercritical phases without encountering any conceptual difficulties.

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II. EQUATIONS OF STATE

A. Van der Waals Equation of State

The van der Waals EOS (vdWEOS) is the basis of various EOSs. The contributions of the vdWEOS are that it laid foundations for modern cubic EOS, radically improved prediction potential, formulated the principle of corresponding states and was the first to predict continuity of matter between gas and liquid. Van der Waals (1973) accounted for the non-zero molecular volume and non-zero force of attraction for a real substance. Van der Waals established that molecules should have an infinite volume and modified the pressure term of the Ideal gas equation to account for molecular interaction [4]. The prediction of liquid behavior became more accurate as the volume approaches a more limiting value, b at high pressures as in (4).

$$\lim_{p \rightarrow \infty} V(p) = b \quad (4)$$

The vdW EOS gives a simple relationship between pressure, temperature and molar volume. Considering the corrections to the ideal gas law, the Van der Waals equation of state is written as in (5).

$$P = RT/(v - b) - \frac{a}{v^2} \quad (5)$$

In (5) P , T , a , R and b are absolute pressure, molar volume, absolute temperature, attraction parameter, universal gas constant and the repulsion parameter. The van der Waals equation is not capable of predicting phase equilibrium accurately.

B. Redlich Kwong Equation

The Redlich Kwong is a cubic equation of state based on the van der Waals equation [5]. It can be applied to mixtures by using mixing rules to the equation of state parameters. It improved the Van der Waals equation with a better description of the attractive term. Redlich and Kwong introduced an adjustment to the van der Waal's attractive

pressure term $\left(\frac{a}{V^2}\right)$ which improved the prediction the prediction vapour phase physical properties. The Redlich-Kwong equation is relatively simple and can predict component or mixture behavior based on little data. Its limitation is that it cannot be used liquid-liquid and vapour-liquid equilibrium prediction but gases only [6].

$$P = \frac{RT}{(v - b)} - \frac{a}{(\sqrt{T} v(v + b))} \quad (6)$$

The constants a and b can be calculated from (7) and (8).

$$a = 0.42748 (R^2 * T_c^{2.5})/P_c \quad (7)$$

$$b = 0.08664 * RT_c/P_c \quad (8)$$

The Redlich-Kwong equation is expressed as in (9).

$$P = \frac{NRT}{(V - bN)} - a \left[\frac{N^2}{T^{1/2} (V + bN)} \right] \quad (9)$$

C. Soave-Redlich Kwong Equation

In 1972, Soave proposed an important modification to the Redlich-Kwong Equation of State (EOS). The modification fitted experimental vapor-liquid data well and could predict phase behavior of mixtures in the critical region. Until the work of soave (1972), modifications to the vdW EOS focused on temperature dependency of the attractive parameter. Soave proposed a two-variable dependency for 'a' as in (10) accounting for the shape of the molecules through the Pitzer's acentric factor (ω) [7].

$$a = a(T, \omega) \quad (10)$$

The Soave-Redlich-Kwong equation of state can accurately describe both liquid and vapor phase behaviour. Various modifications have been proposed to the Soave-Redlich-Kwong equation to improve its accuracy.

$$P = \frac{RT}{(V - b)} - \frac{a\alpha}{v(v + b)} \quad (11)$$

$$\alpha = [1 + S(1 - (T_r))]^2 \quad (12)$$

In (12), T_r is the reduced temperature and S can be calculated from (13).

$$S = 0.48 + 1.574\omega - 0.176\omega^2 \quad (13)$$

The major drawback in the SRK EOS is that the critical compressibility factor takes on the unrealistic universal critical compressibility of 0.333 for all substances. [7] Consequently, the molar volumes are typically overestimated, i.e., densities are underestimated. . Another major drawback of the SRK EOS was the poor liquid density prediction.

D. Peng Robinson Equation

The Peng-Robinson equation of state (1976) was developed to handle both vapor and liquid properties near equilibrium conditions. The development of this equation was focused on natural gas systems [9]. It is generally superior to the Soave Redlich Kwong equation in the prediction of liquid densities.

$$P = \frac{RT}{(v - b)} - \frac{a\alpha}{(v(v + b) + b(b - v))} \quad (14)$$

While they kept the temperature dependency of the attractive term and the acentric factor as introduced by Soave, Peng and Robinson introduced various fitting parameters to describe this dependency.

$$a = 0.45724 (R^2 * T_c^2)/P_c \quad (15)$$

$$\alpha = [1 + S(1 - (\frac{T}{T_c}))]^2 \quad (16)$$

$$S = 0.37464 + 1.54266\omega - 0.26992\omega^2 \quad (17)$$

$$b = 0.07780 * RT_c/P_c \quad (18)$$

Peng and Robinson (1978) suggested (19) for $\omega > 0.49$.

$$S = 0.3796 + 1.4850\omega - 0.1644\omega^2 + 0.01666\omega^3 \quad (19)$$

Equation (20) predicted the vapour pressure of heavy hydrocarbons over a wide temperature range better.

$$P = \frac{\rho NRT}{(1 - b\rho)} - \frac{a\rho^2}{1 + 2b\rho - b^2\rho^2} \quad (20)$$

a and b can be calculated from (21) to (26)

$$a = a_c \omega \quad (21)$$

$$a_c = 0.45724 (R^2 * T_c^2) / P_c \quad (22)$$

$$\alpha = [1 + \kappa(1 - (T_r))]^2 \quad (23)$$

$$T_r = \frac{T}{T_c} \quad (24)$$

$$b = 0.07780 * RT_c / P_c \quad (25)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (26)$$

The Peng-Robinson and Soave-Redlich-Kwong equations are widely used in industry. They are simple to use and accurately represent the relationships temperature, pressure, and phase compositions in binary and multicomponent systems. They only require critical properties and the acentric factor for the generalized parameters. The success of these equations is restricted to the estimation of phase equilibrium pressure as predicted saturated liquid volumes are higher than measured data.

E. The General Equation of State

Starting with $\rho = \rho(\rho, T)$ and $C_p = C_p(\rho, T)$

$$\left(\frac{\partial h}{\partial p} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_p \quad (27)$$

In (27) $v = \frac{1}{\rho}$. The equation of state for enthalpy is presented as in (28).

$$\partial h = C_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right) \right] \quad (28)$$

The user-defined expressions for ρ and C_p must be thermodynamically consistent and this requires that mathematical properties for exact differentials be satisfied. For example if $dz(x,y)$ is an exact differential defined as in (29).

$$dz(x, y) = Mdx + Ndy \quad (29)$$

$$M = \left(\frac{\partial z}{\partial x} \right)_y \quad (30)$$

$$N = \left(\frac{\partial z}{\partial y} \right)_x \quad (31)$$

Consistency requires that:

$$\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y \quad (32)$$

Then the equations of state must obey (33).

$$\left(\frac{\partial C_p}{\partial p} \right) = \frac{\partial}{\partial T} \left(v - T \left[\frac{\partial v}{\partial T} \right] \right)_p \quad (33)$$

F. The Modern Cubic Equation of state

Equation (34) is an example of a cubic equation of state [10] derived from van der Waals equation.

$$v^3 - \left(b + \frac{RT}{\rho} \right) v^2 + \left(\frac{a}{\rho} \right) v - \left(\frac{ab}{\rho} \right) = 0 \quad (34)$$

Introducing the compressibility factor Z ($Z = \frac{PV}{RT}$) into equation (34) we obtain (35).

$$Z^3 - \left(1 - \frac{bP}{RT} \right) Z^2 + \left(\frac{aP}{R^2 T^2} \right) Z - \left(\frac{abP^2}{RT^3} \right) = 0 \quad (35)$$

Cubic equations of state are simple to apply, require few parameters and do not require complex computational techniques. Most modifications and research based on the van der Waals equation of state has focused on improving agreement with experimental data and the modeling of the attractive and repulsive parameters a and b respectively.

G. PR, SRK and RK Comparisons

The Redlich Kwong EOS can satisfactorily be applied for fugacity, enthalpy and entropy departure calculations as well gas phase properties [9]. This equation poorly predicts liquid phase properties. The Peng Robinson EOS performs well for gas and condensate systems compared to the Soave Redlich Kwong. The Soave Redlich Kwong gives excellent predictions for polar systems. The authors wish to test the applicability of the Peng Robinson equation of state in the prediction of phase equilibrium involving volatile organic compounds and polymeric solvents.

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