Equations of States (EOS)

An equation of state (EOS) is an ***analytical expression*** relating the pressure, ***p***, to the temperature, ***T***, and the volume, ***V***.

The main advantage of using an EOS is that ***the same equation*** can be used to model the behavior of all phases, thereby ***assuring consistency when performing phase equilibria calculations***.

The best known and the simplest example of an equation of state is the ideal gas equation, expressed mathematically by the expression

$$p = \frac{RT}{V}$$

$V =$ gas volume in ft^3 per 1 mol of gas, ft^3/mol

Skoltech
Skolkovo Institute of Science and Technology

Equations of States (EOS) - The Van der Waals Equation of State "VdW EOS"

However, the **extreme limitations** of the applicability of the equation is prompted numerous attempts to develop an equation of state suitable for **describing the behavior of real fluids at extended ranges of pressures and temperatures**.

In developing the ideal gas EOS, **two assumptions** were made:

1. *The volume of the gas molecules is insignificant compared to the total volume and distance between the molecules.*
2. *There are no attractive or repulsive forces between the molecules.*

Equations of States (EOS) - VdW EOS - Introduction

Removing of the First Assumption

Removing of the Second Assumption

$$p = \frac{RT}{V} \Longrightarrow p = \frac{RT}{V-b} \Longrightarrow \boxed{p = \frac{RT}{V-b} - \frac{a}{V^2}}$$

Reflect the Volume of Molecules (Rep. term)

Attractive Forces between Molecules(Att. Term)

p = system pressure, psia
T = system temperature, °R
R = gas constant, 10.73 psi-ft^3/lb-mol, °R
V = volume, ft^3/mol
a = "attraction" parameter
b = "repulsion" parameter

The two parameters, ***a and b***, are ***constants*** characterizing the ***molecular properties*** of the ***individual components***.

Equations of States (EOS) - VdW EOS – *a* & *b*

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \xRightarrow{If\ p\ is\ low}$$

The **volume of the gas phase is large** ***in comparison with*** **the volume of the molecules.**

The parameter *b* is negligible.

$\frac{a}{V^2}$ ***becomes insignificant***

VdW approaches to ideal equation

$\xRightarrow{If\ p\ is\ high}$ ***V*** becomes very small and ***approaches the value b***

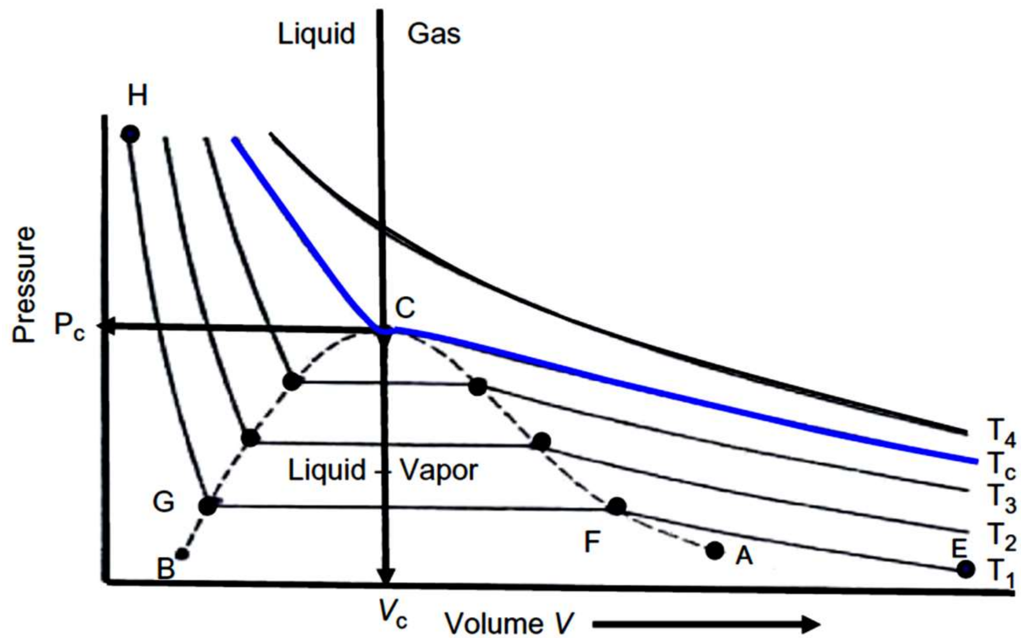
which is the **actual molecular volume** $\lim_{p \to \infty} V(p) = b$

Equations of States (EOS) - VdW EOS – *a* & *b* - *Logic*

It has been ***observed*** that the ***critical isotherm*** has a ***horizontal slope and an inflection point*** at the ***critical point***.

Mathematically:

$$\left[\frac{\partial p}{\partial V}\right]_{T_c,P_c} = 0 \quad \& \quad \left[\frac{\partial^2 p}{\partial V^2}\right]_{T_c,P_c} = 0$$



Equations of States (EOS) - VdW EOS – *a* & *b* – *Calculation I*

$$p=\frac{RT}{V-b}-\frac{a}{V^2}\xRightarrow{\left[\frac{\partial p}{\partial V}\right]_{T_c,P_c}=0\ @\ Critical\ Point}\left[\frac{\partial p}{\partial V}\right]_{T_c,P_c}=\frac{\partial}{\partial V_C}\left(\frac{RT_C}{V_C-b}-\frac{a}{V_C^2}\right)=-RT_C(V_C-b)^{-2}+2aV_C^{-3}$$
$$=0$$

$$\Rightarrow\left[\frac{\boldsymbol{\partial p}}{\boldsymbol{\partial V}}\right]_{\boldsymbol{T_c,P_c}}=-\frac{\boldsymbol{RT_C}}{(\boldsymbol{V_C-b})^2}+\frac{\boldsymbol{2}}{\boldsymbol{aV_C^3}}=\boldsymbol{0}$$

$$\left[\frac{\partial^2 p}{\partial V^2}\right]_{T_c,P_c}=\frac{\partial}{\partial V}\left[\frac{\partial p}{\partial V}\right]_{T_c,P_c}=0\Rightarrow\frac{\partial}{\partial V_C}\left(-RT(V_C-b)^{-2}+2aV_C^{-3}\right)=2RT_C(V_C-b)^{-3}-6aV_C^{-4}=0$$

$$\Rightarrow\left[\frac{\boldsymbol{\partial^2 p}}{\boldsymbol{\partial V^2}}\right]_{\boldsymbol{T_c,P_c}}=\frac{\boldsymbol{2RT_C}}{(\boldsymbol{V_C-b})^3}-\frac{\boldsymbol{6}}{\boldsymbol{aV_C^4}}=\boldsymbol{0}$$

Equations of States (EOS) - VdW EOS – *a* & *b* – *Calculation II*

$$\left.\begin{aligned}\left[\frac{\partial p}{\partial V}\right]_{T_c,P_c} &= -\frac{RT_C}{(V_C-b)^2}+\frac{2}{aV_C^3}=0\\ \left[\frac{\partial^2 p}{\partial V^2}\right]_{T_c,P_c} &= \frac{2RT_C}{(V_C-b)^3}-\frac{6}{aV_C^4}=0\end{aligned}\right\rangle b=\frac{1}{3}V_c \quad \& \quad a=\left(\frac{8}{9}\right)RT_CV_C$$

$$\text{VdW} \Longrightarrow p=\frac{RT}{V-b}-\frac{a}{V^2}\xrightarrow{@Critical\ Point} p_c=\frac{RT_C}{V_C-b}-\frac{a}{V_C^2}\xrightarrow{a=\left(\frac{8}{9}\right)RT_CV_C\ \ \&\ \ b=\frac{1}{3}V_c} p_cV_c=0.375RT_c$$

$$Real\ Gas\ Law \Longrightarrow pV=ZnRT\xrightarrow{@Critical\ Point,\ n=1} p_cV_c=ZRT_c\xrightarrow{Analogy\ with\ VdW} Z\approx 0.375\xleftrightarrow{Experiments}[0.23\sim 0.31]$$

Equations of States (EOS) - VdW EOS – *a* & *b* – *Calculation III*

More convenient and traditional expressions for calculating

$$a = \left(\frac{8}{9}\right) RT_C V_C \quad \& \quad b = \frac{1}{3} V_c$$

$$\xRightarrow{V_c = \frac{0.375 RT_c}{p_c}}$$

$$a = \Omega_a \frac{R^2 T_C^2}{p_C}$$

$$b = \Omega_b \frac{RT_C}{p_C}$$

R = gas constant, 10.73 psia-ft^3/lb-mol-°R
p_c = critical pressure, psia
T_c = critical temperature, °R
$\Omega_a = 0.421875$
$\Omega_b = 0.125$

Equations of States (EOS) - VdW EOS – Volumetric Form I

$$p=\frac{RT}{V-b}-\frac{a}{V^2}\Longrightarrow p-\frac{RT}{V-b}+\frac{a}{V^2}=0\Longrightarrow V^2p-\frac{RT}{V-b}V^2+a=0\Longrightarrow$$

$$V^2p(V-b)-RTV^2+a(V-b)=0\Longrightarrow pV^3-pbV^2-RTV^2+aV-ab=0\Longrightarrow$$

$$pV^3-(pb+RT)V^2+aV-ab=0\Longrightarrow$$

$$V^3-\left(b+\frac{RT}{p}\right)V^2+\left(\frac{a}{p}\right)V-\left(\frac{ab}{p}\right)=0$$

The VdW two-parameter & cubic equation of state

a & b

3 possible V, at least 1 real value

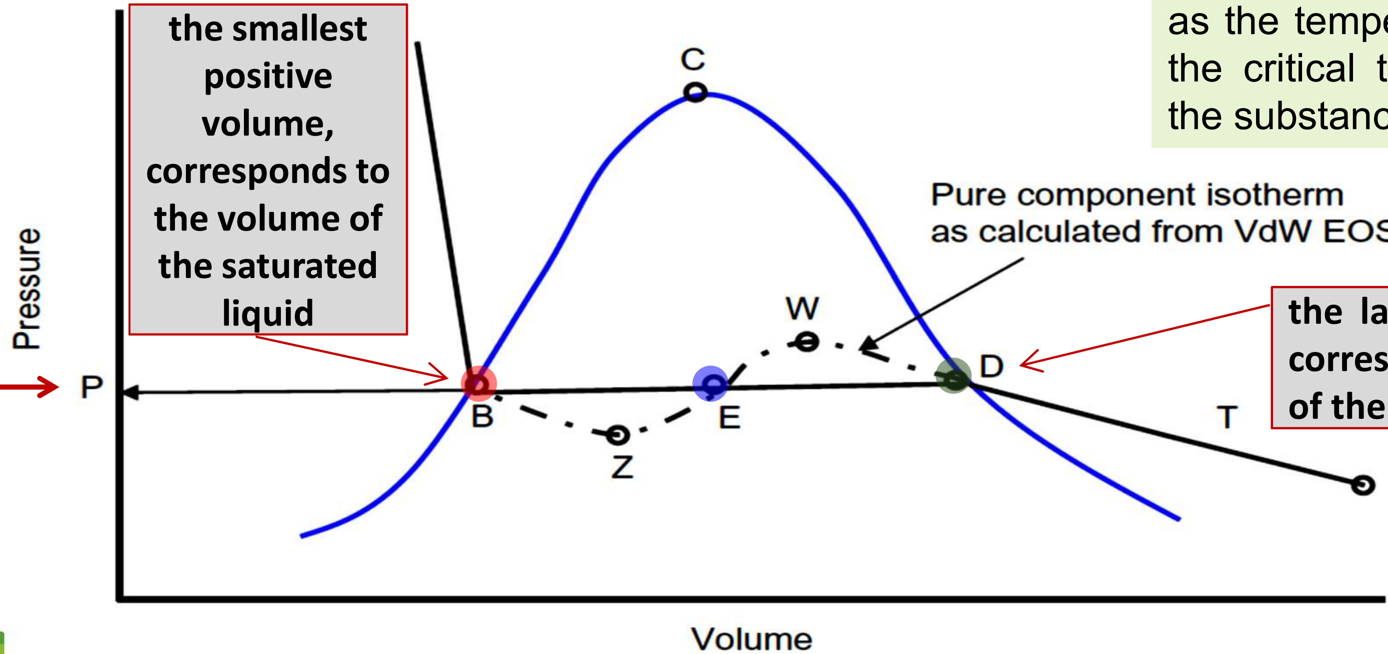
Equations of States (EOS) - VdW EOS – Volumetric Form *II*

The volumetric form of VdW describes the **liquid-condensation phenomenon** and the **passage from the gas to the liquid phase** as the gas is compressed.

It has *3 real roots (volumes)* for each *specified pressure*

These values become identical as the temperature approaches the critical temperature, T_C, of the substance.

the smallest positive volume, corresponds to the volume of the saturated liquid



the largest root (volume), corresponds to the volume of the saturated vapor

Equations of States (EOS) - VdW EOS based on the compressibility factor

$$V^3 - \left(b + \frac{RT}{p}\right)V^2 + \left(\frac{a}{p}\right)V - \left(\frac{ab}{p}\right) = 0 \xRightarrow{V=\frac{ZRT}{p}}$$

$$\left(\frac{ZRT}{p}\right)^3 - \left(b + \frac{RT}{p}\right)\left(\frac{ZRT}{p}\right)^2 + \left(\frac{a}{p}\right)\left(\frac{ZRT}{p}\right) - \left(\frac{ab}{p}\right) = 0 \Rightarrow$$

$$Z^3 - \left(b + \frac{RT}{p}\right)\left(\frac{RT}{p}\right)^2\left(\frac{p}{RT}\right)^3 Z^2 + \left(\frac{a}{p}\right)\left(\frac{RT}{p}\right)\left(\frac{p}{RT}\right)^3 Z - \left(\frac{ab}{p}\right)\left(\frac{p}{RT}\right)^3 = 0 \Rightarrow$$

$$Z^3 - \left(1 + \frac{bp}{RT}\right)Z^2 + \left(\frac{ap}{R^2T^2}\right)Z - \left(\frac{bp}{RT}\right)\left(\frac{ap}{R^2T^2}\right) = 0 \xRightarrow{\left(\frac{ap}{R^2T^2}\right)=A,\left(\frac{bp}{RT}\right)=B}$$

$$Z^3 - (1 + B)Z^2 + (A)Z - BA = 0$$

It has the important application of the density calculation

Equations of States (EOS) - VdW EOS - Example 7

A pure propane is held in a closed container at **100°F**. **Both gas and liquid** are present. Calculate, using the van der Waals EOS, the **density of the gas and liquid** phases.

$$Real\ Gas\ Law \Longrightarrow pV = ZnRT \Longrightarrow pV = Z\frac{m}{M}RT \Longrightarrow pM = Z\rho RT \Longrightarrow$$

$$\boldsymbol{\rho = \frac{pM}{ZRT}}$$

Equations of States (EOS) - VdW EOS - Example 7-Cont.

$$M = 44\ lb/mol$$

$$T = 100 + 460 = 560°R$$

$$R = 10.73\ psi.ft^3/(lbmol.°R)$$

$$p \xRightarrow{Equilibrium} p = p_v \xRightarrow{Cox\ Chart} p_v = 185\ psi$$

$$Z \xRightarrow{for\ Gas\ and\ Liquid} Z^3 - (1 + B)Z^2 + (A)Z - BA = 0$$

Skoltech
Skolkovo Institute of Science and Technology

Equations of States (EOS) - VdW EOS - Example 7-Cont.

$$Z^3 - (1 + B)Z^2 + (A)Z - BA = 0$$

Table 1.1 Physical Properties for Pure Components

	See Note No. →		A	B		C	D	Critical Constants			
Number	Compound	Formula	Molar Mass (Molecular Weight)	Boiling Point (°F) 14.696 psia	Vapor Pressure (psia), 100°F	Freezing Point (°F) 14.696 psia	Refractive Index, n_D 60°F	Pressure (psia)	Temperature (°F)	Volume (ft³/lb-m)	Number
1	Methane	CH_4	16.043	−258.73	(5000)*	−296.44*	1.00042*	666.4	−116.67	0.0988	1
2	Ethane	C_2H_6	30.070	−127.49	(800)*	−297.04*	1.20971*	706.5	89.92	0.0783	2
3	Propane	C_3H_8	44.097	−43.75	188.64	−305.73*	1.29480*	616.0	206.06	0.0727	3

$$A = \frac{ap}{R^2T^2} \Longrightarrow a = \Omega_a \frac{R^2T_C^2}{p_C} = 0.421875 \frac{10.73^2 * 666^2}{616.3} = 34957.4 \xrightarrow{p=p_v} A = 0.179122$$

$$B = \frac{bp}{RT} \Longrightarrow b = \Omega_b \frac{RT_C}{p_C} = 0.125 \frac{10.73 * 666}{616.3} = 1.4494 \xrightarrow{p=p_v} B = 0.044625$$

Equations of States (EOS) - VdW EOS - Example 7-Cont.

$$Z^3 - (1 + B)Z^2 + (A)Z - BA = 0 \xRightarrow{A=0.179122\ ,B=0.044625}$$

$$Z^3 - 1.044625Z^2 + 0.179122Z - 0.007933 = 0$$

$$\xRightarrow{Solve} 3\ Z \xRightarrow{The\ min\ \&\ max} Z^V = 0.72365 \quad \& \quad Z^L = 0.07534$$

$$\rho^V = \frac{pM}{Z^V RT} = 1.87\ {}^{lb}/_{ft^3}$$

$$\rho^L = \frac{pM}{Z^L RT} = 17.98\ {}^{lb}/_{ft^3}$$

Equations of States (EOS) -The Redlich-Kwong Equation of State "RK EOS"

$$VdW \Rightarrow p = \underbrace{\frac{RT}{V-b}}_{\text{Attraction}} - \underbrace{\frac{a}{V^2}}_{\text{Repulsion}}$$

Does not consider the effect of temperature on the intermolecular attractive forces

RK EOS →

$$p = \frac{RT}{V-b} - \frac{a}{V(V+b)\sqrt{T}}$$

Imposing the **critical point conditions** and solving the resulting two equations **simultaneously**

$$a = \Omega_a \frac{R^2 T_C^{2.5}}{p_C} \qquad b = \Omega_b \frac{RT_C}{p_C}$$

$\Omega_a = 0.42747$

$\Omega_b = 0.08664$

Volum. →

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$$

$$A = \frac{ap}{R^2 T^{2.5}}$$

$$B = \frac{bp}{RT}$$

Equations of States (EOS) – RK EOS – Mixing Rules

Redlich and Kwong **extended** the application of their equation to ***hydrocarbon liquid and gas mixtures*** through:

$$a_m = \left[\sum_{i=1}^{n} x_i \sqrt{a_i}\right]^2$$

$$b_m = \sum_{i=1}^{n} [x_i b_i]$$

Or

$$a_m = \left[\sum_{i=1}^{n} y_i \sqrt{a_i}\right]^2$$

$$b_m = \sum_{i=1}^{n} [y_i b_i]$$

$$A = \frac{a_m p}{R^2 T^{2.5}}$$

$$B = \frac{b_m p}{RT}$$

where

n = number of components in the mixture
a_i = Redlich-Kwong a parameter for the ith component
b_i = Redlich-Kwong b parameter for the ith component
a_m = parameter a for mixture
b_m = parameter b for mixture
x_i = mole fraction of component i in the liquid phase

Equations of States (EOS) – RK EOS – Mixing Rules – Example 8

Calculate the density of a crude oil with the composition at ***4000 psia*** and ***160°F*** given in the table below. Use the ***RK EOS***.

Component	x_i	M	p_c	T_c
C_1	0.45	16.043	666.4	343.33
C_2	0.05	30.070	706.5	549.92
C_3	0.05	44.097	616.0	666.06
n-C_4	0.03	58.123	527.9	765.62
n-C_5	0.01	72.150	488.6	845.8
C_6	0.01	84.00	453	923
C_{7+}	0.40	215	285	1287

Equations of States (EOS) – RK EOS – Mixing Rules – Example 8 – Cont.

1

$$a_i = 0.47274\frac{R^2T_c^{2.5}}{p_c}$$

$$b_i = 0.08664\frac{RT_c}{p_c}$$

2

$$a_m = \left[\sum_{i=1}^{n} x_i\sqrt{a_i}\right]^2 = 2{,}591{,}967$$

$$b_m = \sum_{i=1}^{n}[x_i b_i] = 2.0526$$

Component	x_i	M	p_c	T_c	a_i	b_i
C_1	0.45	16.043	666.4	343.33	161,044.3	0.4780514
C_2	0.05	30.070	706.5	549.92	493,582.7	0.7225732
C_3	0.05	44.097	616.0	666.06	914,314.8	1.004725
n-C_4	0.03	58.123	527.9	765.62	1,449,929	1.292629
n-C_5	0.01	72.150	488.6	845.8	2,095,431	1.609242
C_6	0.01	84.00	453	923	2,845,191	1.945712
C_{7+}	0.40	215	285	1287	1.022348 (10^7)	4.191958

Equations of States (EOS) – RK EOS – Mixing Rules – Example 8 – Cont.

3

$$A = \frac{a_m p}{R^2 T^{2.5}} = \frac{2{,}591{,}967(4000)}{10.73^2 (620)^{2.5}} = 9.406539$$

$$B = \frac{b_m p}{RT} = \frac{2.0526(4000)}{10.73(620)} = 1.234049$$

4

$$Z^3 - Z^2 + 6.934845Z - 11.60813 = 0$$

$$Z^L = 1.548126$$

5

$$\rho = \frac{pM}{ZRT} \xrightarrow{Z \to Z^L,\ M \to M_a = \sum x_i M_i = 110.2547}$$

$$\rho^L = \frac{pM_a}{Z^L RT} = \frac{(4000)(100.2547)}{(10.73)(620)(1.548120)} = 38.93\ \mathrm{lb/ft^3}$$

Note that calculating the liquid density is also possible to be done by Standing's method which is an empirical correlation. So why EOS? (Laborious and Inaccurate)

Equations of States (EOS) – The Soave-Redlich-Kwong Equation of State "SRK EOS"

A **significant milestones** in the development of **cubic equations of state** **(Double Solving)**

A more **generalized temperature dependent term**

$$p = \frac{RT}{V-b} - \frac{a\alpha(T)}{V(V+b)}$$

$$a = \Omega_a \frac{R^2 T_c^2}{p_c}$$

$$b = \Omega_b \frac{RT_c}{p_c}$$

$$\Omega_a = 0.42747$$
$$\Omega_b = 0.08664$$

$$\alpha(T) = \left[1 + m\left(1 - \sqrt{T/T_c}\right)\right]^2$$

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$$

At temperatures other than the critical temperature

$$m = 0.480 + 1.74\omega - 0.176\omega^2$$

$$\xRightarrow{\text{Corrected}} \quad m = 0.48508 + 1.55171\omega - 0.15613\omega^2$$

$$A = \frac{(a\alpha)p}{(RT)^2}$$

$$B = \frac{bp}{RT}$$

Skoltech
Skolkovo Institute of Science and Technology

Equations of States (EOS) – SRK EOS – Mixing Rules

$$(a\alpha)_m = \sum_i \sum_j \left[x_i x_j \sqrt{a_i a_j \alpha_i \alpha_j}(1 - k_{ij})\right] \rightarrow A = \frac{(a\alpha)_m p}{(RT)^2}$$

$$b_m = \sum_i [x_i b_i] \rightarrow B = \frac{b_m p}{RT}$$

The parameter k_{ij} is an ***empirically determined correction factor*** called the ***binary interaction coefficient (BIC),*** which is included to characterize any binary system formed by components i and j in the hydrocarbon mixture.

1. $k_{i,j+1} > k_{i,j}$
2. $k_{i,j} = 0$
3. $k_{i,j} = k_{j,i}$
4. $k_{ii} = 0$

$$k_{C_1-C_{7+}} = 0.18 - \frac{16.668\, v_{ci}}{\left[1.1311 + (v_{ci})^{1/3}\right]^6}$$

$$v_{ci} = 0.4804 + 0.06011\, M_i + 0.00001076\,(M_i)^2$$

v_{ci} = critical volume of the C_{7+}, or its lumped component, ft^3/lbm
M_i = molecular weight

Skoltech
Skolkovo Institute of Science and Technology

Equations of States (EOS) – SRK EOS – Example 9

A ***two-phase hydrocarbon system*** exists in equilibrium at ***4000 psia*** and ***160°F***. The system has the composition shown in the following table. Assuming k_{ij} = 0, calculate the density of each phase by using the SRK EOS.

Component	x_i	y_i	p_c	T_c	ω_i
C_1	0.45	0.86	666.4	343.33	0.0104
C_2	0.05	0.05	706.5	549.92	0.0979
C_3	0.05	0.05	616.0	666.06	0.1522
C_4	0.03	0.02	527.9	765.62	0.1852
C_5	0.01	0.01	488.6	845.8	0.2280
C_6	0.01	0.005	453	923	0.2500
C_{7+}	0.40	0.0005	285	1160	0.5200

$$m_{C7} = 215 \ {}^{lb_m}/_{mol}$$

Skoltech
Skolkovo Institute of Science and Technology

Equations of States (EOS) – SRK EOS – Example 9

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

$$a = 0.42747 \frac{R^2 T_c^2}{p_c}$$

$$b = 0.08664 \frac{R T_c}{p_c}$$

Component	p_c	T_c	ω_i	α_i	a_i	b_i
C_1	666.4	343.33	0.0104	0.6869	8689.3	0.4780
C_2	706.5	549.92	0.0979	0.9248	21,040.8	0.7225
C_3	616.0	666.06	0.1522	1.0502	35,422.1	1.0046
C_4	527.9	765.62	0.1852	1.1616	52,390.3	1.2925
C_5	488.6	845.8	0.2280	1.2639	72,041.7	1.6091
C_6	453	923	0.2500	1.3547	94,108.4	1.9455
C_{7+}	285	1160	0.5200	1.7859	232,367.9	3.7838

Equations of States (EOS) – SRK EOS – Example 9 – Cont.

For the **gas phase**:

$$(a\alpha)_m = \sum_i \sum_j \left[y_i y_j \sqrt{a_i a_j \alpha_i \alpha_j} \left(1 - k_{ij}\right) \right] = 9219.3$$

$$b_m = \sum_i [y_i b_i] = 0.5680$$

= 0

For the **liquid phase**:

$$(a\alpha)_m = \sum_i \sum_j \left[x_i x_j \sqrt{a_i a_j \alpha_i \alpha_j} \left(1 - k_{ij}\right) \right] = 104{,}362.9$$

$$b_m = \sum_i [x_i b_i] = 1.8893$$

Equations of States (EOS) – SRK EOS – Example 9 – Cont.

For the **gas phase**:

$$A = \frac{(a\alpha)_m p}{R^2T^2} = \frac{(9219.3)(4000)}{(10.73)^2(620)^2} = 0.8332$$

$$B = \frac{b_m p}{RT} = \frac{(0.5680)(4000)}{(10.73)(620)} = 0.3415$$

$$Z^3 - Z^2 + \left(A - B - B^2\right)Z + AB = 0$$

$$Z^3 - Z^2 + (0.8332 - 0.3415 - 0.3415^2)Z + (0.8332)(0.3415) = 0$$

For the *largest* root $Z^v = 0.9267$

For the **liquid phase**:

$$A = \frac{(a\alpha)_m p}{R^2T^2} = \frac{(104,362.9)(4000)}{(10.73)^2(620)^2} = 9.4324$$

$$B = \frac{b_m p}{RT} = \frac{(1.8893)(4000)}{(10.73)(620)} = 1.136$$

$$Z^3 - Z^2 + \left(A - B - B^2\right)Z + AB = 0$$

$$Z^3 - Z^2 + (9.4324 - 1.136 - 1.136^2)Z + (9.4324)(1.136) = 0$$

For the *smallest* root $Z^L = 1.4121$

Skoltech
Skolkovo Institute of Science and Technology

Equations of States (EOS) – The Peng-Robinson Equation of State "PR EOS"

As a basis for creating **an improved model**, Peng and Robinson (PR) proposed the following expression

$$p = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)+b(V-b)}$$

$$a = \Omega_a \frac{R^2 T_c^2}{p_c}$$

$$b = \Omega_b \frac{RT_c}{p_c}$$

$$\Omega_a = 0.45724$$

$$\Omega_b = 0.07780$$

$$\alpha(T) = \left[1 + m\left(1 - \sqrt{T/T_c}\right)\right]^2$$

$$Z^3 + (B-1)Z^2 + \left(A - 3B^2 - 2B\right)Z - \left(AB - B^2 - B^3\right) = 0$$

$$m = 0.3796 + 1.54226\omega - 0.2699\omega^2.$$

$$\xRightarrow{If\ \omega > 0.49}$$

$$m = 0.379642 + 1.48503\omega - 0.1644\omega^2 + 0.016667\omega^3$$

$$A = \frac{(a\alpha)_m p}{(RT)^2}$$

$$B = \frac{b_m p}{RT}$$

$$(a\alpha)_m = \sum_i \sum_j \left[x_i x_j \sqrt{a_i a_j \alpha_i \alpha_j}\left(1 - k_{ij}\right)\right]$$

$$b_m = \sum_i \left[x_i b_i\right]$$

Equations of States (EOS) – PR EOS – Mixing Rules

Component	CO_2	N_2	H_2S	C_1	C_2	C_3	i-C_4	n-C_4	i-C_5	n-C_5	C_6	C_7	C_8	C_9	C_{10}
CO_2	0	0	0.135	0.105	0.130	0.125	0.120	0.115	0.115	0.115	0.115	0.115	0.115	0.115	0.115
N_2		0	0.130	0.025	0.010	0.090	0.095	0.095	0.100	0.100	0.110	0.115	0.120	0.120	0.125
H_2S			0	0.070	0.085	0.080	0.075	0.075	0.070	0.070	0.070	0.060	0.060	0.060	0.055
C_1				0	0.005	0.010	0.035	0.025	0.050	0.030	0.030	0.035	0.040	0.040	0.045
C_2					0	0.005	0.005	0.010	0.020	0.020	0.020	0.020	0.020	0.020	0.020
C_3						0	0.000	0.000	0.015	0.015	0.010	0.005	0.005	0.005	0.005
i-C_4							0	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
n-C_4								0	0.005	0.005	0.005	0.005	0.005	0.005	0.005
i-C_5									0	0.000	0.000	0.000	0.000	0.000	0.000
n-C_5										0	0.000	0.000	0.000	0.000	0.000
C_6											0	0.000	0.000	0.000	0.000
C_7												0	0.000	0.000	0.000
C_8													0	0.000	0.000
C_9														0	0.00
C_{10}															0

Equations of States (EOS) – Volume Shift – SRK & PR EOS

A **comparison** of the **predicted** liquid molar volume by leading ***two parameter EOS*** with **experimental** data of **pure compounds** generally shows a systematic deviation.

$$V^{L}_{corr} = V^{L} - \sum_i (x_i c_i)$$

$$V^{v}_{corr} = V^{v} - \sum_i (y_i c_i)$$

$$c_i = (0.0115831168 + 0.411844152\omega_i)\left(\frac{T_{ci}}{p_{ci}}\right)$$

Component	PR EOS	SRK EOS
N_2	−0.1927	−0.0079
CO_2	−0.0817	0.0833
H_2S	−0.1288	0.0466
C_1	−0.1595	0.0234
C_2	−0.1134	0.0605
C_3	−0.0863	0.0825
i-C_4	−0.0844	0.0830
n-C_4	−0.0675	0.0975
i-C_5	−0.0608	0.1022
n-C_5	−0.0390	0.1209
n-C_6	−0.0080	0.1467
n-C_7	0.0033	0.1554
n-C_8	0.0314	0.1794
n-C_9	0.0408	0.1868
n-C_{10}	0.0655	0.2080

Equations of States (EOS) – Volume Shift – SRK & PR EOS – Example 10

Rework Example 9 by incorporating volume corrections.

$$c_i = (0.0115831168 + 0.411844152\omega_i)\left(\frac{T_{ci}}{p_{ci}}\right)$$

Component	x_i	p_c	T_c	ω_i	c_i	$c_i x_i$	y_i	$c_i y_i$
C_1	0.45	666.4	343.33	0.0104	0.00839	0.003776	0.86	0.00722
C_2	0.05	706.5	549.92	0.0979	0.03807	0.001903	0.05	0.00190
C_3	0.05	616.0	666.06	0.1522	0.07729	0.003861	0.05	0.00386
C_4	0.03	527.9	765.62	0.1852	0.1265	0.00379	0.02	0.00253
C_5	0.01	488.6	845.8	0.2280	0.19897	0.001989	0.01	0.00198
C_6	0.01	453	923	0.2500	0.2791	0.00279	0.005	0.00139
C_{7+}	0.40	285	1160	0.5200	0.91881	0.36752	0.005	0.00459
$\sum$						0.38564		0.02349

$$V^{v} = \frac{RTZ^{v}}{p} = \frac{(10.73)(620)(0.9267)}{4000} = 1.54119\,\text{ft}^3/\text{mol}$$

$$V^{L} = \frac{RTZ^{L}}{p} = \frac{(10.73)(620)(1.4121)}{4000} = 2.3485\,\text{ft}^3/\text{mol}$$

$$V^{L}_{\text{corr}} = V^{L} - \sum_i (x_i c_i) = 2.3485 - 0.38564 = 1.962927\,\text{ft}^3/\text{mol}$$

$$V^{v}_{\text{corr}} = V^{v} - \sum_i (y_i c_i) = 1.54119 - 0.02394 = 1.5177\,\text{ft}^3/\text{mol}$$

Equations of States (EOS) – Volume Shift – SRK & PR EOS – Example 10 – Cont.

$$Z^{v}_{corr} = \frac{(4000)(1.5177)}{(10.73)(620)} = 0.91254$$

$$Z^{L}_{corr} = \frac{(4000)(1.962927)}{(10.73)(620)} = 1.18025$$

$$\rho = \frac{pM_a}{RTZ}$$

$$\rho^{v} = \frac{(4000)(20.89)}{(10.73)(620)(0.91254)} = 13.767 \text{ lb/ft}^3$$

$$\rho^{L} = \frac{(4000)(100.25)}{(10.73)(620)(1.18025)} = 51.07 \text{ lb/ft}^3$$

Equations of States (EOS) – Summary

EOS	$p_{repulsion}$	$p_{attraction}$	a	b
Ideal	$\frac{RT}{V}$	0	0	0
vdW	$\frac{RT}{V-b}$	$\frac{a}{V^2}$	$\Omega_a \frac{R^2 T_c^2}{p_c}$	$\Omega_b \frac{RT_c}{p_c}$
RK	$\frac{RT}{V-b}$	$\frac{a}{V(V+b)\sqrt{T}}$	$\Omega_a \frac{R^2 T_c^{2.5}}{p_c}$	$\Omega_b \frac{RT_c}{p_c}$
SRK	$\frac{RT}{V-b}$	$\frac{a\alpha(T)}{V(V+b)}$	$\Omega_a \frac{R^2 T_c^2}{p_c}$	$\Omega_b \frac{RT_c}{p_c}$
PR	$\frac{RT}{V-b}$	$\frac{a\alpha(T)}{V(V+b)+b(V-b)}$	$\Omega_a \frac{R^2 T_c^2}{p_c}$	$\Omega_b \frac{RT_c}{p_c}$