12. EQUATIONS OF STATE

Equations of state (EOS) are, for pure substances, mathematical relations between volume, pressure, and temperature. For mixtures, EOS in addition include composition. EOS are very versatile tools for engineering applications. They can be used for all states of matter (mostly gas, vapor, and liquid), and they can describe transitions between states.

The development of EOS for the representation of real systems started in 1873 with the Publication of the van der Waals (vdW) EOS. [1] Since then hundreds of different EOS have been proposed. It is beyond the scope to review in detail all these developments. In fact, all of the oil/gas pressure-volume-temperature and phase equilibria computations are based on one equation of state. For broad reviews of EOS, the reader is referred to [2] - Abott (1979), [3] - Leland (1980), and [4] - Tsonopoulos and Heidman (1986). In addition [5] - Tzouvaras (1986) gives a particularly clear and detailed account of the different types of EOS.

12.1. TYPES OF EQUATIONS OF STATE

Leland (1980) [3] distinguished between four families of EOS:
1. van der Waals (vdW) family
2. Benedict-Webb-Rubin (BWR) family
3. Reference-fluid equations
4. Augmented-rigid-body equations

The vdW family encompasses simple, mostly cubic EOS. Their main characteristic is the separation between the repulsive and attractive effects. Despite their simplicity, these EOS display quantitatively correct performance, even being able to describe multiphase equilibria, tricritical points, and other complicated phenomena ([6] - Michelsen and Heidemann, 1988). Cubic EOS are discussed further in the next section.

The Benedict-Webb-Rubin (BWR) family includes complicated EOS and are empirical extensions of the virial EOS. Besides the Benedict-Webb-Rubin (1940) [7] EOS itself, the most significant members of this family for oil/gas application are the Starling (1973) EOS [8], and the Lee and Kesler (1975) EOS [9].

The reference-fluid equations aim at accurate representation of a large amount of PVT data for pure substances. The equations contain many parameters. An important application of reference-fluid equations is their use as reference fluids in corresponding state theories, see e.g., Mollerup and Rowlinson (1974) [10].

The augmented-rigid-body family combines description of repulsive forces between hard molecules of different shapes with expressions for the molecular attractions. The sound theoretical basis of the repulsive term is the most important and promising characteristic of these EOS. The Carnahan and Starling (1972) [11] expression for the repulsion between hard spheres has been repeatedly used. Approximations to the augmented-rigid-body EOS include simplifications of the expression for the repulsive term, such as in the Cubic-Chain-of-Rotators EOS ([12] - Kim et al., 1986).

Today all four families of EOS receive considerable attention. Recent literature, however, mainly contains developments in EOS of the vdW family, because of their simplicity and practicality, and of the augmented-rigid body EOS, because of their theoretical foundation and potential for accurate extensions.

The oil/gas PVT- and phase equilibrium computations in this book are based on a cubic equation of the vdW family. The reasons for this choice are:

1. Cubic EOS of the vdW family yield relatively simple expressions for the thermodynamic properties and phase equilibrium relationships of interest.

2. The EOS of the other three families, though more complicated in nature, do not give quantitatively better descriptions of mixture phase transitions than do cubic EOS ([3] - Tsonopoulos and Heidman, 1986).

It is well known that the more complicated EOS yield better predictions of liquid densities than the cubic EOS. This disadvantage of the cubic EOS is taken into account.

12.1.1 . CUBIC EQUATIONS OF STATE

Cubic EOS are explicit regarding pressure and may be written in terms of a repulsive and an attractive contribution to the pressure P:

$$P = P^{rep} - P^{attr} \tag{12.1}$$

Classical examples of cubic EOS are those of van der Waals (vdW) (1873) [1]:

$$P = \frac{RT}{(V - b)} - \frac{a}{V^2} \tag{12.2}$$

and Redlich and Kwong (R-K) (1940) [13]:

$$P = \frac{RT}{(V - b)} - \frac{a}{[T^{0.5} \cdot V(V + b)]} \tag{12.3}$$

where

R = gas constant
T = temperature
V = molar volume

There are two parameters;

b − represents the "real," or hard-sphere volume of the molecules
a − represents the intermolecular attraction.

The parameters a and b in Eq. 12.2 and Eq. 12.3 are normally determined by imposing the critical conditions:

$$\left[\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0\right]_{crit.point} \tag{12.4}$$

The vdW and R-K EOS may be extended by altering their temperature-dependence and by including parameters in addition to a and b.

Jensen (1987) [14] defines two generalized cubic EOS, from which many of the commonly used equations may be derived:

Type 1: The repulsive-term modified R-K EOS

$$P = \frac{RT\,(2V + b_1)(T)}{V\big(2V - b_2(T)\big)} - \frac{a(T)}{\big(V + b_3(T)\big)} \tag{12.5}$$

Type 2: The attractive-term modified vdW EOS

$$P = \frac{RT}{\big(V - b_1(T)\big)} - \frac{a(T)}{\big(V + b_2(T)\big)\big(V + b_3(T)\big)} \tag{12.6}$$

Eq. 12.5 and Eq. 12.6 each contain four temperature-dependent parameters: a, b_1, b_2, and b_3. Some of the EOS that may be derived from Eq. 12.5 and Eq. 12.6 are:

Soave-Redlich-Kwong (SRK), ([15] - Soave, 1972):

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

(12.7)

Type 2: $a = a(T)$, $b_1 = b$, $b_2 = 0$, $b_3 = b$

The Peng-Robinson EOS (PR), ([16] - Peng and Robinson, 1976)

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

(12.8)

Type 2: $a = a(T)$, $b_1 = b$, $b_2 = (1 + 2^{0.5})b$, $b_3 = (1 - 2^{0.5})b$

The Adachi-Lu-Sugie EOS (ALS), ([17] - Adachi et al., 1983)

$$P = \frac{RT}{(V-b_1)} - \frac{a(T)}{(V-b_2)(V+b_3)}$$

(12.9)

Peneloux's modified SRK EOS, ([18] Peneloux et al., 1982)

$$P = \frac{RT}{(V-b)} - \frac{a(T)}{(V+c)(V+b+2c)}$$

(12.10)

Type 2: : $a = a(T)$, $b_1 = b$, $b_2 = c$, $b_3 = (b+2c)$

The Ishikawa-Chung-Lu EOS, ([19] Ishikawa et al., 1980)

$$P = \frac{RT\left(2V + b(T)\right)}{V\left(2V - b(T)\right)} - \frac{a(T)}{T^{0.5}V\left(V + b(T)\right)}$$

(12.11)

Type 1: $a = a(T)$, $b_1 = b(T)$, $b_2 = b(T)$, $b_3 = b(T)$

Many more examples exist ([14] - Jensen, 1987). The presence of parameters in addition to a and b as in the R-K and vdW EOS permits inclusion of constraints other than those given by Eq. 12.4. Careful evaluations informed the choice to base the oil/gas computations on the SRK EOS. No other cubic EOS tested yielded better results for naturally occurring oil and gas mixtures.

12.1.2. THE SRK-EQUATION OF STATE

The analytical form of the Soave-Redlich-Kwong (SRK)-equation of state [15] is given in Eq. 12.7. The a and b parameters are found from the pressure-volume relationship at the critical point expressed in Eq. 12.4. By inserting the expression for the pressure given in Eq. 12.7 into Eq. 12.4 the following relations may be derived for the pure component a-parameter at the critical point and for the pure component b-parameter:

$$a_{ci} = 0.42747 \cdot R^2 \cdot \frac{T_{ci}^2}{P_{ci}}$$

(12.12)

$$b_i = 0.08664 \cdot R \cdot \frac{T_{ci}}{P_{ci}}$$

(12.13)

Values for T_c and P_c of some common petroleum mixture constituents are given in Tbl. 12.1 .

Tbl. 12.1. Critical Temperature (T_c), Critical Pressure (P_c) and Acentric Factor (ω)
of Some Common Petroleum Mixture Constituents

	T_c (K)	P_c (atm)	ω
N2	126.2	33.5	0.040
CO2	304.2	72.8	0.225
H2S	373.2	88.2	0.100
C1	190.6	45.4	0.008
C2	305.4	48.2	0.098
C3	369.8	41.9	0.152
i-C4	408.1	36.0	0.176
n-C4	425.2	37.5	0.193
i-C5	460.4	33.4	0.227
n-C5	469.5	33.3	0.251
n-C6	507.4	29.3	0.296

The temperature dependence of the a -parameter entering Eq. 12.7 is expressed in the form of a term $\alpha_i(T)$ which multiplied with a_{ci} gives the final expression for the a -parameter of the SRK-equation:

$$a_i(T) = a_{ci}\alpha_i(T) \tag{12.14}$$

The a parameter is obtained from the following expression:

$$\alpha_i(T) = \left(1 + m_i\left(1 - T_{ri}^{0.5}\right)\right)^2 \tag{12.15}$$

where

$$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2 \tag{12.16}$$

It is seen from Eq. 12.15 that $\alpha_i(T) = 1$ at the critical temperature, where a therefore becomes equal to a_{ci}. In Eq. 12.15 ω_i is the acentric factor which is defined as follows [20] (Pitzer, 1955):

$$\omega_i = -\log_{10} P_{ri}^{vap} \ (at \ T_{ri} = 0.7) - 1 \tag{12.17}$$

where P_{ri}^{vap} is the reduced vapor pressure (P/P_{ci}) of component i.

The acentric factor may be interpreted as the non-sphericity of molecules of type i. Values for ω_i of a number of different components are given in Tbl. 12.1. The dependence of m_i on ω_i given in Eq. 12.16 is found from experimental vapor pressure data for aliphatic hydrocarbons ranging from C1 to C10 ([15] Soave, 1972).

For a mixture, a and b are found as follows:

$$a = \sum_i \sum_j z_i z_j a_{ij} \tag{12.18}$$

$$b = \sum_i z_i b_i \tag{12.19}$$

where z_i and z_j are mole fractions of components i and j, respectively and:

$$a_{ij} = \left(a_i a_j\right)^{1/2}\left(1 - k_{ij}\right) \tag{12.20}$$

k_{ij} is a binary interaction coefficient, which is usually considered equal to zero for hydrocarbon-hydrocarbon interactions, and different from zero for interactions between a hydrocarbon and a non-hydrocarbon, and between unlike pairs of non-hydrocarbons. Tbl. 12.2 shows the non-zero binary interaction coefficients to be recommended for use with the SRK-equation [21] (Reid et al., 1977) for some lighter petroleum mixture constituents.

Tbl. 12.2. Non-Zero Binary Interaction Coefficients for use with the SRK-EOS
between common Petroleum Mixture Constituents. [21] (Reid et al., 1977)

Component Pair	N_2	CO_2	H_2S
N_2	0.00	0.00	0.00
CO_2	0.00	0.00	0.12
H_2S	0.00	0.12	0.00
C1	0.02	0.12	0.08
C2	0.06	0.15	0.07
C3	0.08	0.15	0.07
i-C4	0.08	0.15	0.06
n-C4	0.08	0.15	0.06
i-C5	0.08	0.15	0.06
n-C5	0.08	0.15	0.06
n-C6	0.08	0.15	0.05

Eq. 12.7 can be rewritten in terms of the compressibility factor, Z:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \qquad (12.21)$$

where Z is defined as:

$$Z = \frac{PV}{RT} \qquad (12.22)$$

and A and B are given by the following expressions:

$$A = \frac{a(T)P}{R^2T^2} \qquad (12.23)$$

$$B = \frac{bP}{RT} \qquad (12.24)$$

The polynomial of Eq. 12.21 may have one or three real roots. When for a pure component or a single-phase mixture only one real root exists, this root equals the compressibility factor of the phase present. The compressibility factor of a dilute gas is close to unity. The compressibility factor of a near critical pure component is close to 0.33. Using the SRK-equation of state the compressibility factor of a pure component at the critical point will always be found equal to 0.33. In the case where the polynomial of Eq. 12.21 has three real roots, one or more phases may be found.

In the case of two phases, each component will have equal fugacities, f_i, in both phases:

$$f_i^V = f_i^L \qquad (12.25)$$

where V and L refer to the vapor and liquid phases, respectively. The criterion of equal fugacities indicates equality in the driving forces in the transfer of components from one phase to the other. The fugacity is related to the chemical potential, μ, as follows:

$$\mu_i = \mu_i^0 + RT \ ln \ f_i \qquad (12.26)$$

where μ_i^0 is a standard-state chemical potential for component i. Eq. 12.25 can be rewritten:

$$\phi_i^V y_i = \phi_i^L x_i \ \ or \ K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V} \qquad (12.27)$$

where:

   x_i = mole fractions of component i in liquid phase
   y_i = mole fractions of component i in vapour phase
   ϕ_i = fugacity coefficient

$K_i = \frac{y_i}{x_i}$ is called the equilibrium ratio. The following general thermodynamic relationship exists for determination of the fugacity coefficient of component i in the mixture:

$$\ln \phi_i = -\frac{1}{RT} \int_{\infty}^{V} \left(\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right) dV - \ln Z \qquad (12.28)$$

where n_i is the number of moles of type i. When the SRK-equation is used Eq. 12.28 yields:

$$\ln \phi_i = \frac{b_i}{b}(Z - 1) - \ln Z + \ln \left(\frac{V}{V - b} \right)$$
$$+ \frac{a}{bRT} \left[\frac{b_i}{b} - 2 \sum_j \frac{z_j(1 - k_{ij})(a_i a_j)^{0.5}}{a} \right] \ln \left(\frac{V + b}{V} \right) \qquad (12.29)$$

The phase compositions are related to the total composition as follows:

$$x_i = \frac{z_i}{(1 + (K_i - 1)\beta)} \qquad (12.30)$$

$$y_i = \frac{K_i z_i}{(1 + (K_i - 1)\beta)} \qquad (12.31)$$

where:

z_i = mole fraction of component i in the total mixture

β = the molar vapor phase fraction

The SRK-equation may also be used for calculation of other thermodynamic properties, e.g., the enthalpy and the entropy. The enthalpy, H of a pure component, or a mixture of given composition, may be calculated as the sum of two contributions, namely the ideal gas enthalpy (H^{id}) and the residual enthalpy (H^{res}):

$$H = H^{id} + H^{res} \qquad (12.32)$$

and similarly, for the entropy:

$$S = S^{id} + S^{res} \qquad (12.33)$$

The ideal gas terms at temperature T are usually calculated from the following equations:

$$H^{id} = \sum_i z_i H_i^{id} = \sum_i z_i \int_{T_{ref}}^{T} C_P^{id} \, dT \qquad (12.34)$$

$$S^{id} = \sum_i z_i \left(S_i^{id} - R \ln z_i \right) = \sum_i z_i \left(\int_{T_{ref}}^{T} \left(\frac{C_P^{id}}{T} \right) dT - R \ln \left(\frac{P}{P_{ref}} \right) - R \ln z_i \right) \qquad (12.35)$$

where :

T_{ref} is a reference temperature, here 0 °C.

P_{ref} is the reference pressure, here 1 atm.

C_P^{id} the ideal gas heat capacity,

which is usually approximated by a third-degree polynomial in the temperature

$$C_P^{id} = C_1 + C_2 T + C_3 T^2 + C_4 T^3 \qquad (12.36)$$

Values for the coefficients $C_1 - C_4$ of the lighter petroleum mixture constituents are given by Reid et al., (1977) [21]. The residual terms of Eq. 12.32 and Eq. 12.33 may be derived from the SRK-equation using the following general thermodynamic relations:

$$H^{res} = -RT^2 \frac{\partial \ln \phi}{\partial T} \qquad (12.37)$$

where ϕ is the fugacity coefficient of the mixture and the derivative is taken at constant pressure and total composition. Also

$$S^{res} = \frac{H^{res}}{T} - R \ln \phi \qquad\qquad (12.38)$$

A summary of the equations used for computing the thermodynamic properties from the SRK equation of state is shown in the box:

Summary of Equations Used for Calculating Fugacity Coefficients, Enthalpies and Entropies from the SRK-EOS [22] (Edmister and Lee, 1984)

Soave-Redlich-Kwong (SRK) - EOS (Soave, 1972) [15]:

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

$$a_i(T) = a_{ci}\alpha_i(T)$$

$$\alpha_i(T) = \left(1 + m_i\left(1 - T_{ri}^{0.5}\right)\right)^2$$

$$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2$$

$$a_{ci} = 0.42747\, R^2 \frac{T_{ci}^2}{P_{ci}}$$

$$b_i = 0.8664\, R\, \frac{T_{ci}}{P_{ci}}$$

$$a = \sum_i \sum_j (a_i a_j)^{0.5}\, z_i z_j \left(1 - k_{ij}\right)$$

$$b = \sum_i z_i b_i$$

Fugacity coefficient at constant composition, ϕ:

$$\ln\phi = Z - 1 - \ln(Z - B) - \left(\frac{A}{B}\right)\left(1 + \frac{B}{Z}\right)$$

$$Z = \frac{PV}{RT}\ ;\quad \frac{B}{Z} = \frac{b}{V}\ ;\quad \frac{A}{B} = \frac{a}{bRT}$$

Fugacity coefficient of component i in a mixture, ϕ_i:

$$\ln\phi_i = -\ln(Z-B) + (Z-1)\frac{b_i}{b} - \frac{A}{B}\left[\frac{1}{a}\left(2a_i\sum_j z_j a_j^{0.5}\left(1-k_{ij}\right)\right) - \frac{b_i}{b}\ln\left(1 + \frac{B}{Z}\right)\right]$$

Enthalpy at constant composition, H:

$$H^{id} = \sum_i z_i H_i^{id} \qquad \text{(id means ideal gas)}$$

$$H_i^{id} = \int_{T_{ref}}^{T} C_P^{id}\, dT$$

$$H^{res} = RT\left[z - 1 - \frac{A}{B}\left(1 - \frac{T}{a}\frac{da}{dT}\right)\ln\left(1 - \frac{B}{Z}\right)\right]$$

$$T\frac{da}{dT} = -\sum_i \sum_j z_i z_j m_j \left(a_i a_{cj} T_{rj}\right)^{0.5}\left(1 - k_{ij}\right)$$

$$H = H^{id} + H^{res}$$

Entropy at constant composition, S;

$$S^{id} = \sum_i z_i\left(S_i^{id} - R\ln z_i\right) = \sum_i z_i\left(\int_{T_{ref}}^{T}\left(\frac{C_P^{id}}{T}\right)dT - R\ln\left(\frac{P}{P_{ref}}\right) - R\ln z_i\right)$$

$$S^{res} = \ln(Z-B) + \frac{A}{B}\left[\frac{T}{a}\frac{da}{dT}\right]\ln\left(1 - \frac{B}{Z}\right)$$

$$S = S^{id} + S^{res}$$

12.2. PHASE DENSITIES

The phase densities may be determined from the SRK-equation by using Eq. 12.7 or Eq. 12.21. In general, good results are obtained for vapor phase densities, whereas the liquid phase densities are somewhat underestimated [23] (Pedersen et ah, 1984). Using the SRK-equation for density calculations in cases where the liquid phase densities are of importance is therefore not recommended.

It is generally advantageous to use the same density correlation for both gas and liquid phases (e.g., to avoid discontinuities in the near critical region).

12.2.1 Peneloux method

Peneloux et al. (1982) [18] have presented a consistent method for correction of SRK-volumes using an equation of state of the following form:

$$P = \frac{RT}{(V - b)} - \frac{a}{(V + c)(V + b + 2c)}$$
(12.39)

where c is a constant, which for a mixture is calculated as follows:

$$c = \sum_i c_i z_i$$
(12.40)

c_i is the value of c for component i. The SRK-equation (Eq. 12.7), and Eq. 12.39 give identical results for saturation points and K-factors, but different results for gas and liquid phase volumes. The SRK-volume, $\tilde{V}$, and the Peneloux-volume, V, are related as follows:

$$V = \tilde{V} - c$$
(12.41)

The parameter c can therefore be regarded as a volume translation parameter. Martin (1979) [24] has a discussion on the volume translation concept.

For non-hydrocarbons and for hydrocarbons < C7 the following expression is used for c:

$$c_i = 0.40768 \frac{RT_{ci}}{P_{ci}} (0.29441 - (Z_{RA})_i)$$
(12.42)

where $(Z_{RA})_i$ is the Racket compressibility factor [25] (Spencer and Banner, 1973) of component i for which the following approximation is used:

$$(Z_{RA})_i = 0.29056 - 0.08775 \, \omega_i$$
(12.43)

Peneloux et al. (1982) [18] suggest finding the c -value of paraffinic, naphthenic, and aromatic C7+-components, respectively, from fifth-degree polynomials in the carbon number. Pedersen et al. (1984) [23] have found that this procedure works reasonably well for gas and gas condensate mixtures, while inaccurate results are obtained for heavy oil mixtures. The c -parameter of C7+ -components (or fractions) may instead be found as the difference in the results for the molar volume at atmospheric pressure and 15°C, calculated with the SRK-equation and determined experimentally (Pedersen et al, 1988) [26].

Far from the critical point it is of less importance to get consistent results for gas and liquid phase densities. Liquid density correlations developed specifically for petroleum mixtures are then often superior to the Peneloux [18] procedure. Examples of such procedures follow.

12.2.2. The Alani-Kennedy Equation

The form of the Alani-Kennedy equation (1960) [27] is:

$$V^3 - \left(\frac{RT}{P} + b\right)V^2 + \frac{aV}{P} - \frac{ab}{P} = 0 \tag{12.43}$$

For pure substances:

$$a = K \exp\left(\frac{n}{T}\right) \tag{12.43}$$

and

$$b = mT + C \tag{12.43}$$

where K, n, m, and C are constants. Values for the lighter hydrocarbons are given in Tbl. 12.3. It is suggested using the methane values also for N_2, CO_2, and H_2S.

Tbl. 12.3. Constants of the Alani-Kennedy Equation for Pure Hydrocarbons [27]

Component	K	n	$m \cdot 10^4$	C
C1 (70-300°F)	9160.6413	61.893223	3.3162472	0.50874303
C1 (301-460°F)	147.47333	3247.4533	-14.072637	1.8326695
C2 (100-249°F)	46709.573	-404.48844	5.1520981	0.52239654
C2 (250-460°F)	17495.343	34.163551	2.8201736	0.62309877
C3	20247.757	190.24420	2.1586448	0.90832519
i-C4	32204.420	131.63171	3.3862284	1.1013834
n-C4	33016.212	146.15445	2.9021257	1.1168144
n-C5	37046.234	299.62630	2.1954785	1.4364289
n-C6	52093.006	254.56097	3.6961858	1.5929406

Units: P in psia; T in °R; V in ft³/lb-mol; R = 10.7335 lb-ft³/(in.)² °R lb-mol.
Source: Alani and Kennedy (1960) [27].

The values of a and b of a C7+-fraction are found from the following expressions:

$$\begin{aligned} \ln a_{C7+} = {} & 3.8405985 \cdot 10^{-3} M_{C7+} - 9.5638281 \cdot 10^{-4} \frac{M_{C7+}}{\rho_{C7+}} + \frac{2.6180818 \cdot 10^2}{T} \\ & + 7.3104464 \cdot 10^{-6}(M_{C7+})^2 + 10.753517 \end{aligned} \tag{12.47}$$

$$\begin{aligned} b_{C7+} = {} & 3.4992740 \cdot 10^{-2} M_{C7+} - 7.2725403 \cdot \rho_{C7+} + 2.2323950 \cdot 10^{-4} T \\ & - 1.6322572 \cdot 10^{-2} \frac{M_{C7+}}{\rho_{C7+}} + 6.2256545 \end{aligned} \tag{12.48}$$

where

   M_{C7+} = molecular weight of the total C7+-fraction

   ρ_{C7+} = density (in g/cm³) of the total C7+-fraction at 1 atm and 15°C

a and b of a mixture are found as molar averages. The Alani-Kennedy equation [27] gives accurate results for liquid densities, but it is not applicable to vapor phase densities.

12.2.3. The Standing-Katz Procedure [28]

This was originally developed as a graphical procedure (Standing and Katz, 1941) [28].

The Standing-Katz procedure gives accurate density results for liquid phases with a large concentration of heavy components. The procedure is not applicable to vapor phases.

The analytical solutions are described in the compendium.

Analytical expressions [23] (Pedersen et al., 1984) approximating the graphical form permit the correlations to be applied in computer calculations also. Further information could be looked up in the book Properties of oils and natural gases (K. S. Pedersen, A. Fredenslund & P. Thomassen).

12.2.4. The API Method

Calculation of the liquid density using the API method (1982) involves the following steps:

1. Calculation of the pseudocritical temperature (pT_c) and pressure (pP_c) for the mixture in question. These values are obtained as molar averages of the pure component critical temperatures and pressures.

2. Calculation of the pseudo reduced temperature (pT_r) and the pseudo reduced pressure (pP_r):

$$pT_r = \frac{T}{T_c}$$
$$pP_r = \frac{P}{P_c}$$

3. Calculation of the average density for the mixture at 60°F and 1 atm from the following formula:

$$\rho_L = \frac{\sum_{n=1}^{n} x_i \cdot M_i}{\sum_{n=1}^{n} \frac{x_i \cdot M_i}{\rho_i}} \tag{12.49}$$

Tbl. 12.5 API Pure Component Densities (ρ) at 1 atm and 15°C.

Component	Density ρ, (g/cm^3)
N2	0.804
CO2	0.809
H2S	0.834
C1	0.300
C2	0.356
C3	0.508
i-C4	0.563
n-C4	0.584
i-C5	0.625
n-C5	0.631
C6	0.664

ρ values for non-hydrocarbons and for C1 - C6 are given in Tbl. 12.5. The measured densities at standard conditions are used for the C7+-components.

4. Calculation of the density correlation factor, C, at standard conditions and at the actual conditions. C is given by the following expression:

$$C = A_1 + A_2 \cdot pT_r + A_3 \cdot (pT_r)^2 + A_4 \cdot (pT_r)^3 \tag{12.50}$$

Each of the coefficients $A_1 - A_4$ in Eq. 12.50 is determined by an expression of the following form:

$$A_i = B_1 + B_2 \cdot pP_r + B_3 \cdot (pP_r)^2 + B_4 \cdot (pP_r)^3 + B_5 \cdot (pP_r)^4 \tag{12.51}$$

where the B_i values are given in Tbl. 12.6.

Tbl. 12.6. Coefficients of Eq. 12.51 for Calculation of Liquid Densities Using the API-Method (API (1982).

	B_1	B_2	B_3	B_4	B_5
A_1	1.6368	-0.04615	$2.1138(10^{-3})$	$-0.7845(10^{-5})$	$-0.6923(10^{-6})$
A_2	-1.9693	0.21874	$-8.0028(10^{-3})$	$-8.2328(10^{-5})$	$5.2604(10^{-6})$
A_3	2.4638	-0.36461	$12.8763(10^{-3})$	$14.8059(10^{-5})$	$-8.6895(10^{-6})$
A_4	-1.5841	0.25136	$-11.3805(10^{-3})$	$9.5672(10^{-5})$	$2.1812(10^{-6})$

5. Calculation of the unknown density from the equation:

$$\rho = \rho_L \frac{C_1}{C_2} \tag{12.52}$$

where the C_1 and C_2 are the density correlation factors (Eq. 12.50) at standard conditions, and at the actual conditions, respectively.

The API-density method is only applicable to liquid phases.

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