

A New Thermodynamic Function for Phase-Splitting at Constant Temperature, Moles, and Volume

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DOI 10.1002/aic.12387

Published online August 31, 2010 in Wiley Online Library (wileyonlinelibrary.com).

*We introduce a new thermodynamic function for phase-split computations at constant temperature, moles, and volume. The new volume function F_i introduced in this work is a natural choice under these conditions. Phase equilibrium conditions in terms of the volume functions are derived using the Helmholtz free energy. We present a numerical algorithm to investigate two-phase equilibrium based on the fixed point iteration and Newton method. We demonstrate usefulness and powerful features of the new thermodynamic function for a number of examples in two-phase equilibrium calculations. © 2010 American Institute of Chemical Engineers *AIChE J*, 57: 1897–1904, 2011*
Keywords: two-phase equilibrium, constant volume flash, VT-flash, Helmholtz free energy, volume function

Introduction

Consider a closed system of constant volume V in which there is a mixture of c components with mole numbers n_1, \dots, n_c at temperature T . Assuming that the system is in two-phase, we want to establish compositions and amounts of both phases. This is the problem of two-phase phase-split (the so called flash) under the constant temperature, moles, and volume (VT-flash). The motivation for constant volume flash is the equilibrium calculation in a PVT cell in two-phase when two nonequilibrium phases are introduced.^{1,2} These cells are used to determine diffusion coefficients in both phases in two-phase state. We have found out that the use of conventional methods is based on ad hoc approaches.

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The standard problem of constant pressure and temperature (PT-flash) is addressed in many references.^{3–6} In this approach, pressure, temperature, and overall chemical composition are given. The phase compositions and molar densities are computed using the minimization of the Gibbs energy. This approach has the shortcoming that it cannot provide an answer when a single component is in two-phase region at temperature T and saturation pressure $P = P^{\text{sat}}(T)$ because the chemical potentials of the component in both phases are the same. Therefore, we cannot determine whether the component at these specific conditions is vapor or liquid or a mixture of both. Although P and T are the most preferred variables in chemical engineering, we see that specifying pressure and temperature is not sufficient for the unique determination of the state of the system in this case.

The issue can be resolved by reformulating the problem using the minimization of the Helmholtz free energy rather than Gibbs free energy. In this formulation, the volume of

the system, mole numbers, and temperature are given, and the chemical compositions, molar densities of the phases, and pressure in the mixture are computed. The selection of variables V , T , and n_i , ($i \in \{1, \dots, c\}$) is natural for pressure-explicit equations of state. Unlike in PT-flash, the VT-flash provides a unique answer in any physically admissible situation because when V is known, P can be evaluated readily from say a cubic equation of state. Therefore, we develop a new “volume-based” formulation of equilibrium thermodynamics. The presented derivations lead to a new function F_i , called volume function that plays an analogous role to fugacity that is used in the pressure-based formulation. We present all derivations in details to show that this approach is much more fit for the pressure-explicit equations of state than the standard development using the Gibbs free energy that suffers from the nonuniqueness of volume at given pressure.

A theoretical possibility of other state function-based flash specification (including VT-flash) is mentioned in Refs. 6 and 7, where a nested optimization approach is proposed. This means that in an outer loop we search iteratively for pressure, which is used in PT-flash in the inner loop to evaluate equilibrium state at that pressure. The goal of the iterations is to find a pressure for which the volume constraint is satisfied. This procedure allows to use existing implementations of the PT-flash but, on the other hand, is computationally expensive as it requires many solutions of PT-flashes before the true pressure is found. In this article, we offer an alternative formulation allowing to formulate VT-flash directly without using nested iterations.

The article is structured as follows. In the first section, we introduce the new thermodynamic volume function F_i of variables V , T , and n_i that will be useful in describing thermodynamic behavior of real mixtures under the constant temperature, volume, and moles. Then, we develop an expression for the chemical potential of a component in a mixture in terms of this new function. We reformulate the two-phase equilibrium conditions at constant temperature, volume, and moles using F_i . Next, we propose a numerical algorithm for computation of VT-flash, and, finally, we present examples showing results of phase-equilibrium computations based on the new formulation for a number of mixtures in two-phase state.

Volume Function Coefficient

We will introduce a new thermodynamic volume function that will be useful to derive basic expressions for the chemical potential of a component in a multicomponent mixture from the bulk phase equilibrium thermodynamics. Our derivation will be based on Helmholtz free energy and will use volume, temperature, and moles as primary variables.

Assuming a pressure-explicit equation of state, it is convenient to describe the system using the Helmholtz free energy $A = A(V, T, n_1, \dots, n_c)$. The general expression for the Helmholtz free energy of a bulk phase is given by

$$A = -PV + \sum_{i=1}^c n_i \mu_i, \quad (1)$$

where $P = P(V, T, n_1, \dots, n_c)$ is the pressure given by an equation of state, and $\mu_i = \mu_i(V, T, n_1, \dots, n_c)$ is the chemical potential of the i -th component in the mixture. From

Algorithm: Two-Phase VT-Flash Using Fixed Point Iteration

1. Let c , z_1, \dots, z_c , and $T > 0$ be given. Evaluate $P_0 = P(1/c, T, z_1, \dots, z_c)$, initialize K_i 's using Wilson correlation,⁸ i.e.

$$\ln K_i = 5.37(1 + \omega_i) \left[1 - \frac{T_{ci}}{T} \right] + \ln \frac{P_{ci}}{P_0}$$

at the initial pressure P_0 and set the number of iterations, $n = 0$.

2. Evaluate $\alpha \in (0; 1)$ by solving the Rachford-Rice equation

$$\sum_{i=1}^c \frac{(K_i^n - 1)z_i}{1 + (K_i^n - 1)\alpha} = 0,$$

that can be solved, e.g., by Newton's method.

3. Update chemical compositions of both phases by

$$x'_{i,n+1} = \frac{z_i}{1 + (K_i^n - 1)\alpha}, \quad x''_{i,n+1} = \frac{z_i K_i^n}{1 + (K_i^n - 1)\alpha},$$

4. Use bisection or other method to find $S'_{n+1} \in (0; 1)$ satisfying

$$P \left(\frac{1 - S'_{n+1}}{c(1 - \alpha)}, T, x'_{1,n+1}, \dots, x'_{c,n+1} \right) = P \left(\frac{S'_{n+1}}{c\alpha}, T, x''_{1,n+1}, \dots, x''_{c,n+1} \right),$$

and update the other saturation and molar concentrations by

$$S'_{n+1} = 1 - S''_{n+1}, \quad c'_{n+1} = \frac{c(1 - \alpha)}{1 - S''_{n+1}}, \quad c''_{n+1} = \frac{c\alpha}{S''_{n+1}}.$$

5. Update K_i values by

$$K_i^{n+1} = \frac{c'_{n+1} \Phi_i(1, T, c''_{n+1} x''_{1,n+1}, \dots, c''_{n+1} x''_{c,n+1})}{c''_{n+1} \Phi_i(1, T, c'_{n+1} x'_{1,n+1}, \dots, c'_{n+1} x'_{c,n+1})}.$$

6. Check for convergence. If needed, increase n by one and go to step 2.

$$dA = -SdT - PdV + \sum_{i=1}^c \mu_i dn_i,$$

we see that

$$P = -\frac{\partial A}{\partial V}, \quad \mu_i = \frac{\partial A}{\partial n_i}. \quad (2)$$

Assuming that A is a smooth function of its variables, the mixed second-order derivatives must be interchangeable, which implies

$$\frac{\partial \mu_i}{\partial V} = -\frac{\partial P}{\partial n_i}, \quad (3)$$

with appropriate variables held constant. Integrating (3) between two volumes V_1 and V_2 , we derive the following expression describing the change of chemical potential with volume at constant temperature and moles

$$\mu_i(V_2, T, n_1, \dots, n_c) = \mu_i(V_1, T, n_1, \dots, n_c) - \int_{V_1}^{V_2} \frac{\partial P}{\partial n_i}(V, T, n_1, \dots, n_c) dV. \quad (4)$$

For an ideal gas mixture, the equation of state

$$P = \frac{nRT}{V}, \quad \text{where } n = \sum_{i=1}^c n_i$$

can be integrated using (4) to yield

$$\mu_i(V_2, T, n_1, \dots, n_c) = \mu_i(V_1, T, n_1, \dots, n_c) - RT \ln \frac{V_2}{V_1}. \quad (5)$$

For real mixtures a more general equation than (5) must be used. To simplify our derivations, it is convenient to have a similar form of the expression for the chemical potential of a component in a real mixture as in the ideal case. For this purpose, we introduce the volume function of i -th component $F_i = F_i(V, T, n_1, \dots, n_c)$ by the following properties

$$\begin{aligned} \mu_i(V_2, T, n_1, \dots, n_c) &= \mu_i(V_1, T, n_1, \dots, n_c) \\ &\quad - RT \ln \frac{F_i(V_2, T, n_1, \dots, n_c)}{F_i(V_1, T, n_1, \dots, n_c)}, \end{aligned} \quad (6)$$

and

$$\lim_{V \rightarrow +\infty} \frac{F_i(V, T, n_1, \dots, n_c)}{V} = 1. \quad (7)$$

Furthermore, we define the volume function coefficient by

$$\Phi_i(V, T, n_1, \dots, n_c) = \frac{F_i(V, T, n_1, \dots, n_c)}{V}. \quad (8)$$

Equation 7 then amounts to saying that $\lim_{V \rightarrow +\infty} \Phi_i(V, T, n_1, \dots, n_c) = 1$ for given temperature and moles. The volume function F_i and volume function coefficient Φ_i play analogous roles to fugacity and fugacity coefficients. Comparing (6) with (4), we have

$$RT \ln \frac{F_i(V_2, T, n_1, \dots, n_c)}{F_i(V_1, T, n_1, \dots, n_c)} = \int_{V_1}^{V_2} \frac{\partial P}{\partial n_i}(V, T, n_1, \dots, n_c) dV.$$

Setting $V_1 = V$, the last equation can be rearranged to

$$\begin{aligned} \ln \frac{F_i(V, T, n_1, \dots, n_c)}{V} &= \frac{V_2}{V_2 F_i(V_2, T, n_1, \dots, n_c)} \\ &= -\frac{1}{RT} \int_V^{V_2} \frac{\partial P}{\partial n_i}(V, T, n_1, \dots, n_c) dV. \end{aligned}$$

The above equation can be written as

$$\begin{aligned} \ln \frac{F_i(V, T, n_1, \dots, n_c)}{V} &= \int_V^{V_2} \left[\frac{1}{V} - \frac{1}{RT} \frac{\partial P}{\partial n_i}(V, T, n_1, \dots, n_c) \right] dV \\ &\quad + \ln \frac{F_i(V_2, T, n_1, \dots, n_c)}{V_2}. \end{aligned}$$

Passing $V_2 \rightarrow +\infty$, the last term on the right hand side vanishes because of (7), which yields

$$\ln \Phi_i(V, T, n_1, \dots, n_c) = \int_V^{+\infty} \left[\frac{1}{V} - \frac{1}{RT} \frac{\partial P}{\partial n_i}(V, T, n_1, \dots, n_c) \right] dV. \quad (9)$$

The integral on the right hand side can be evaluated analytically using an equation of state. It follows from (9) that for an ideal gas $F_i(V, T, n_1, \dots, n_c) = V$, and $\Phi_i(V, T, n_1, \dots, n_c) = 1$ for any given temperature, moles, and volume. Thus, the volume function coefficient can indicate the degree of nonideality of a component in the mixture. These properties are “volume-based” counterparts of analogous properties of the fugacity and fugacity coefficients with respect to pressure.

Comparing the integral on the right hand side of (9) with the formula for fugacity coefficients found in literature (see e.g., Ref. 3), we note that the relationship between the volume function coefficient and the fugacity coefficient is

$$\Phi_i = \frac{1}{Z\varphi_i},$$

where φ_i denotes the conventional fugacity coefficient and Z is the phase compressibility factor. Z and φ_i must now be expressed in terms of volume, temperature, and moles. In the literature, the Z and φ_i are usually understood as functions of P , T , and composition. However, when Z and φ are to be evaluated for given P , T , and moles, one has to solve the cubic equation to get volume, which may not be unique, and in that case, one has to select one of the roots based on the Gibbs free energy criteria or other methods. In this article, we present an alternative formulation, which uses the volume function coefficients rather than fugacity coefficients. In this formulation, the root-selection problems do not appear because all functions are expressed in terms of volume, temperature, and moles.

The formula for the volume function coefficient Φ_i for the Peng-Robinson equation⁹ is presented in the Appendix.

Chemical Potential of a Component in a Real Mixture

In the new framework, we describe the dependency of the chemical potential of a component in a real mixture to the chemical potential in a pure substance. An ideal mixture is the one which obeys

$$\mu_i(V, T, n_1, \dots, n_c) = \mu_i(V, T, 0, \dots, 0, n_i, 0, \dots, 0).$$

To simplify the notation, we will denote the chemical potential of the pure substance i as

$$\mu_i^*(V, T, n_i) = \mu_i(V, T, 0, \dots, 0, n_i, 0, \dots, 0),$$

and the volume function in the pure component as

$$F_i^*(V, T, n_i) = F_i(V, T, 0, \dots, 0, n_i, 0, \dots, 0).$$

Equation 6 can be written for the mixture as well as for the pure component

$$\begin{aligned}\mu_i(V, T, n_1, \dots, n_c) &= \mu_i(V_1, T, n_1, \dots, n_c) \\ &\quad - RT \ln \frac{F_i(V, T, n_1, \dots, n_c)}{F_i(V_1, T, n_1, \dots, n_c)}, \\ \mu_i^*(V, T, n_i) &= \mu_i^*(V_1, T, n_i) - RT \ln \frac{F_i^*(V, T, n_i)}{F_i^*(V_1, T, n_i)}.\end{aligned}$$

Subtracting the second expression from the first above,

$$\begin{aligned}\mu_i(V, T, n_1, \dots, n_c) - \mu_i^*(V, T, n_i) \\ &= \mu_i(V_1, T, n_1, \dots, n_c) - \mu_i^*(V_1, T, n_i) \\ &\quad - RT \ln \frac{F_i(V, T, n_1, \dots, n_c)}{F_i(V_1, T, n_1, \dots, n_c)} - RT \ln \frac{F_i^*(V_1, T, n_i)}{F_i^*(V, T, n_i)}.\end{aligned}$$

If the volume V_1 is sufficiently large, the mixture at volume V_1 behaves ideally. Passing $V_1 \rightarrow +\infty$, one can derive

$$\mu_i(V, T, n_1, \dots, n_c) = \mu_i^*(V, T, n_i) - RT \ln \frac{F_i(V, T, n_1, \dots, n_c)}{F_i^*(V, T, n_i)}. \quad (10)$$

Let us assume that we have a mixture at two states $(V', T, n'_1, \dots, n'_c)$ and $(V'', T, n''_1, \dots, n''_c)$. Our goal is to express the difference of chemical potentials between these two states in terms of the volume functions. Using (10), we derive

$$\begin{aligned}\mu_i(V', T, n'_1, \dots, n'_c) - \mu_i(V'', T, n''_1, \dots, n''_c) \\ &= \mu_i^*(V', T, n'_i) - \mu_i^*(V'', T, n''_i) \\ &\quad - RT \ln \frac{F_i(V', T, n'_1, \dots, n'_c)}{F_i(V'', T, n''_1, \dots, n''_c)} + RT \ln \frac{F_i^*(V', T, n'_i)}{F_i^*(V'', T, n''_i)}.\end{aligned}$$

The first two terms on the right hand side can be rewritten as

$$\begin{aligned}\mu_i^*(V', T, n'_i) - \mu_i^*(V'', T, n''_i) &= \mu_i^*(V'/n'_i, T, 1) - \mu_i^*(V''/n''_i, T, 1) \\ &= -RT \ln \frac{F_i^*(V', T, n'_i) n''_i}{F_i^*(V'', T, n''_i) n'_i},\end{aligned}$$

where we take advantage of the fact that the chemical potential is a homogeneous function of order zero and the volume function is a homogeneous function of order one in the volume and moles. Combining the last two equations, we obtain the following key expression for the difference of chemical potentials at two different states written in terms of the volume functions

$$\begin{aligned}\mu_i(V', T, n'_1, \dots, n'_c) - \mu_i(V'', T, n''_1, \dots, n''_c) \\ &= -RT \ln \frac{n''_i F_i(V', T, n'_1, \dots, n'_c)}{n'_i F_i(V'', T, n''_1, \dots, n''_c)}. \quad (11)\end{aligned}$$

Conditions for Two-Phase Equilibrium

Consider a mixture of c components with mole numbers n_1, \dots, n_c occupying volume V at temperature T . Assuming that the mixture will split into two phases, we want to calculate volumes V' and V'' , and mole numbers of each component in each phase n'_i and n''_i for $i = 1, \dots, c$, and consequently the pressure. The equilibrium state is derived from the minimization of the total Helmholtz energy of the mixture

$$A = A(V', T, n'_1, \dots, n'_c) + A(V'', T, n''_1, \dots, n''_c),$$

which is subject to the following constraints

$$V' + V'' = V, \quad (12)$$

and

$$n'_i + n''_i = n_i, \quad i = 1, \dots, c. \quad (13)$$

Using the Lagrange multiplier method, one can find the necessary conditions of the phase equilibria

$$P(V', T, n'_1, \dots, n'_c) = P(V'', T, n''_1, \dots, n''_c), \quad (14)$$

and

$$\mu_i(V', T, n'_1, \dots, n'_c) = \mu_i(V'', T, n''_1, \dots, n''_c), \quad i = 1, \dots, c, \quad (15)$$

as expected. An equivalent expression of (15) in terms of the volume functions reads as

$$\frac{n'_i}{F_i(V', T, n'_1, \dots, n'_c)} = \frac{n''_i}{F_i(V'', T, n''_1, \dots, n''_c)}. \quad (16)$$

Numerical Algorithm for Two-Phase Flash Computation

In two-phase, we are interested to calculate phase compositions, amounts, and also the pressure of the system. Let us rewrite the two-phase flash Eqs. 12–15 in terms of concentrations and compositions of both phases. We introduce the overall molar concentration $c = n/V$, the phase molar concentrations $c' = n'/V'$ and $c'' = n''/V''$, overall mole fractions $z_i = n_i/n$, and phase mole fractions $x'_i = n'_i/n'$ and $x''_i = n''_i/n''$, and phase volume fractions $S' = V'/V$, and $S'' = V''/V$, respectively. Using this notation, Eq. 12 transforms to

$$S' + S'' = 1, \quad (17)$$

whereas the mole balance Eq. 13 can be rewritten as

$$c' x'_i S' + c'' x''_i S'' = c z_i, \quad i = 1, \dots, c. \quad (18)$$

As pressure is an intensive property (homogeneous function of order zero in variables V, n_1, \dots, n_c), Eq. 14 yields

$$P(1, T, c' x'_1, \dots, c' x'_c) = P(1, T, c'' x''_1, \dots, c'' x''_c). \quad (19)$$

Finally, the chemical equilibrium Eq. 16 can be written in terms of the volume function coefficients using (11) as

$$\frac{c' x'_i}{\Phi_i(1, T, c' x'_1, \dots, c' x'_c)} = \frac{c'' x''_i}{\Phi_i(1, T, c'' x''_1, \dots, c'' x''_c)}. \quad (20)$$

To solve these equations using the fixed point iteration (also called successive substitution iteration, SSI), it is convenient to introduce the K_i values by

$$K_i = \frac{x''_i}{x'_i}. \quad (21)$$

From (21) it follows that $x''_i = K_i x'_i$, which can be substituted into (18) to obtain

Table 1. Properties of the Components for the C₁-nC₅ Mixture Used in Examples 1 and 2

Component	ω_i [-]	T_{crit} [K]	P_{crit} [MPa]	M_w [g mol ⁻¹]
C ₁	0.011	190.56	4.599	16
nC ₅	0.251	469.70	3.37	72.2

The C₁-nC₅ binary interaction coefficient is $\delta_{\text{C}_1\text{-nC}_5} = 0.041$.

$$x'_i = \frac{z_i}{1 + (K_i - 1)\alpha}, \quad x''_i = \frac{z_i K_i}{1 + (K_i - 1)\alpha}, \quad (22)$$

where $\alpha = c''S''/c$ is the mole fraction of the double-primed phase. These equations can be used to evaluate phase compositions provided that K_i and α are given. As compositions of both phases in (22) should sum to one, for a given set of K_i values, α can be updated by solving the Rachford-Rice equation¹⁰

$$\sum_{i=1}^c (x''_i - x'_i) = \sum_{i=1}^c \frac{(K_i - 1)z_i}{1 + (K_i - 1)\alpha} = 0. \quad (23)$$

Once α and chemical composition of both phases are established, phase molar concentrations and saturations must be determined so that the pressures in both phases are the same. The following system of four equations

$$\begin{aligned} c'S' &= c(1 - \alpha), \\ c''S'' &= c\alpha, \\ S' + S'' &= 1, \\ P\left(\frac{1}{c'}, T, x'_1, \dots, x'_c\right) &= P\left(\frac{1}{c''}, T, x''_1, \dots, x''_c\right), \end{aligned}$$

for the 4 unknowns (c' , c'' , S' , and S'') can be readily reduced into a single equation for one unknown saturation $S'' \in (0;1)$

$$P\left(\frac{1 - S''}{c(1 - \alpha)}, T, x'_1, \dots, x'_c\right) = P\left(\frac{S''}{c\alpha}, T, x''_1, \dots, x''_c\right). \quad (24)$$

For a cubic equation of state, Eq. 24 is an algebraic equation of the fifth order. In theory it may have up to five real roots. In all examples we examined, there was always only one root in the interval (0;1), which could be readily approximated using the bisection method. Other methods, like the Newton method, can be used as well.

Finally, K_i values are updated using (20) as

$$K_i = \frac{x''_i}{x'_i} = \frac{c'\Phi_i(1/c'', T, x''_1, \dots, x''_c)}{c''\Phi_i(1/c', T, x'_1, \dots, x'_c)}.$$

The key steps of the method are summarized in the Algorithm.

Table 2. Overall Properties of the Mixture and Resulting Phase Properties in Two-Phase Flash at Constant Temperature $T = 371$ K and Volume for Example 1

Property	Unit	Overall mixture	Phase 1	Phase 2
Molar concentration	mol m ⁻³	6307.21	8616.72	4307.03
C ₁ mole fraction	-	0.547413	0.388095	0.823458
nC ₅ mole fraction	-	0.452587	0.611905	0.176542
Phase volume fraction	-		0.464113	0.535887

Table 3. Overall Properties of the Mixture and Resulting Phase Properties in Two-Phase Flash at Constant Temperature $T = 310.95$ K and Volume for Example 2

Property	Unit	Overall mixture	Phase 1	Phase 2
Molar concentration	mol m ⁻³	6135.3	10105.5	3177.77
C ₁ mole fraction	-	0.489575	0.293471	0.954131
nC ₅ mole fraction	-	0.510425	0.706529	0.0458693
Phase volume fraction	-		0.42691	0.57309

The iterations are stopped whenever

$$\max_{i \in \{1, \dots, c\}} |\ln K_i^{n+1} - \ln K_i^n| < \text{tol} = 10^{-12}.$$

Numerical Examples

We have tested the algorithm in several examples of binary and multicomponent mixtures in two-phase. Below we show performance of the method for two binary mixtures and one four-component mixture. Further, we provide two more-complex phase-split computations for a multicomponent reservoir fluid. All examples are motivated by experiments in the PVT cells. In these experiments, the total volume is fixed. A part of this volume is filled by a liquid at some initial pressure P_{ini} . The rest of the volume is filled by a gas at the same initial pressure. When the two fluids are mixed, the pressure changes. The final equilibrium pressure P of the system after mixing results from the VT-flash computation. The correctness of the VT-flash results is checked by performing the PT-flash at the final pressure with the same overall composition and temperature. The agreement was excellent in all cases.

Example 1

In the first example, we investigate two-phase equilibrium for a binary mixture of methane (C₁) and n-pentane (nC₅) of total concentration $c = 6307.21$ mol m⁻³, with mole fractions $z_{\text{C}_1} = 0.547413$ and $z_{\text{nC}_5} = 0.452587$ at temperature $T = 371$ K. The condition corresponds to the PVT-cell experiment in which C₁ (34.4% of volume) is placed on the top of nC₅ at the initial pressure $P_{\text{ini}} = 15$ MPa. Parameters of the Peng-Robinson equation of state are presented in Table 1. The algorithm found a solution in 46 iterations. Within each iteration the Rachford-Rice, Eq. 23, was solved by Newton's method with the initial guess $\alpha = 0.5$. The resulting pressure is $P = 10.4653$ MPa. The overall mixture and phase-split results are summarized in Table 2. The results were verified by the PT-flash computation performed at the final pressure with the same overall composition and temperature. The PT-flash converged in 45 iterations.

Table 4. Properties of the Components for the Four-Component Mixture Used in Example 3

Component	ω_i [-]	T_{crit} [K]	P_{crit} [MPa]	M_w [g mol ⁻¹]
N ₂	0.039	126.21	3.39	28
C ₁	0.011	190.56	4.599	16
C ₃	0.153	369.83	4.248	44.1
nC ₁₀	0.489	617.70	2.110	142.3

Table 5. Binary Interaction Coefficients for the Four-Component Mixture Used in Example 3

Component	N ₂	C ₁	C ₃	nC ₁₀
N ₂	0	0.1	0.1	0.1
C ₁	0.1	0	0.036	0.052
C ₃	0.1	0.036	0	0
nC ₁₀	0.1	0.052	0	0

Example 2

In this example, we compute two-phase equilibrium for a mixture of methane (C₁) and n-pentane (nC₅) of total concentration $c = 6135.3 \text{ mol m}^{-3}$, with mole fractions $z_{C_1} = 0.489575$ and $z_{nC_5} = 0.510425$ at temperature $T = 310.95 \text{ K}$. The condition corresponds to the PVT-cell experiment in which C₁ (65% of volume) is placed on the top of nC₅ at the initial pressure $P_{ini} = 10.2 \text{ MPa}$. Parameters of the Peng-Robinson equation of state are presented in Table 1. The algorithm found a solution in 20 iterations. The resulting pressure is $P = 6.95477 \text{ MPa}$. The overall mixture and split-phase results are summarized in Table 3. The agreement with the PT-flash at the final pressure is excellent. The PT-flash converged in 19 iterations.

Example 3

In Example 3, we compute two-phase equilibrium for a four-component mixture of nitrogen (N₂), methane (C₁), propane (C₃), and n-decane (nC₁₀) at temperature $T = 393.15 \text{ K}$. Here, nitrogen (35% of volume) is placed on the top of a four-component mixture ($z_{N_2} = 0.01$, $z_{C_1} = 0.29$, $z_{C_3} = 0.29$, and $z_{nC_{10}} = 0.41$) at the initial pressure 13.73 MPa. Parameters of the Peng-Robinson equation of state are presented in Tables 4 and 5. The overall molar concentration and overall mole fractions of all components are shown in Table 6. The algorithm found a solution in 25 iterations. The resulting pressure is $P = 14.9502 \text{ MPa}$. Note the pressure increase due to vaporization. The overall mixture and split-phase results are summarized in Table 6. The results agree with those obtained using the PT-flash at the final pressure. The PT-flash converged in 25 iterations.

Example 4

In Example 4, we compute two two-phase equilibria for a multicomponent oil mixed with nitrogen (N₂), and carbon dioxide (CO₂). The oil is modelled using seven components. The composition of the oil and parameters of the Peng-Robinson equation of state are presented in Tables 7 and 8. The

Table 6. Overall Properties of the Mixture and Resulting Phase Properties in Two-Phase Flash at Constant Temperature $T = 393.15 \text{ K}$ and Volume for Example 3

Property	Unit	Overall mixture	Phase 1	Phase 2
Molar concentration	mol m ⁻³	5912.74	6690.98	4795.04
N ₂ mole fraction	-	0.2463	0.12944	0.48049
C ₁ mole fraction	-	0.2208	0.15509	0.35248
C ₃ mole fraction	-	0.2208	0.25349	0.15529
nC ₁₀ mole fraction	-	0.3121	0.46198	0.01173
Phase volume fraction	-		0.58952	0.41048

Table 7. Composition and Properties of the Components for the Reservoir Fluid Used in Example 4

Component	z_i	$\omega_i [-]$	$T_{crit} [\text{K}]$	$P_{crit} [\text{MPa}]$	$M_w [\text{g mol}^{-1}]$
N ₂	0.0003	0.0390	126.21	3.390	28.0
CO ₂	0.0140	0.2390	304.14	7.375	44.0
C ₁	0.5634	0.0110	190.56	4.599	16.0
PC ₁	0.1970	0.1113	333.91	5.329	34.64
PC ₂	0.0770	0.2344	456.25	3.445	69.52
PC ₃	0.0845	0.4470	590.76	2.376	124.57
C ₁₂₊	0.0638	0.9125	742.58	1.341	248.30

pseudocomponents are defined as PC₁ (H₂S + C₂ + C₃), PC₂ (C₄-C₆), and PC₃ (C₇-C₁₁). In both experiments, 50% of volume of the PVT cell is filled by this oil. The initial pressure $P_{ini} = 30.34 \text{ MPa}$, and the temperature is $T = 413.71 \text{ K}$. Under these conditions, the oil is in single phase with molar concentration $c_{oil} = 8944.22 \text{ mol m}^{-3}$. The remaining 50% of volume is filled with either N₂ or CO₂ at the same initial pressure. Addition of gas turns the system into two phase in both cases.

For the case of N₂, the overall properties of the resulting mixture and phase-split results are summarized in Table 9. The final pressure is $P = 32.66 \text{ MPa}$. The algorithm found a solution in 33 iterations. The results agree with those obtained using the PT-flash at the final pressure. The PT-flash converged in 34 iterations. Some of the K_i -values in Table 9 are very different from one; the system is far from the critical point.

For the case of CO₂, the overall properties of the resulting mixture and split-phase results are summarized in Table 10. The final pressure is $P = 31.27 \text{ MPa}$. The algorithm found a solution in 266 iterations. The results agree with those obtained using the PT-flash at the final pressure. The PT-flash converged in 254 iterations. The K_i -values in Table 10 are closer to one. Unlike in the previous case, the mixture is near-critical, which explains the increased number of iterations that are needed to converge using the fixed point iteration method.

Summary and Conclusions

In this work, we have introduced a new thermodynamic function to describe two-phase equilibrium at constant temperature, volume, and moles. The new volume function coefficient replaces the fugacity coefficients that are used in common formulations of two-phase equilibrium at constant temperature and pressure. Unlike the conventional approach, our method can determine uniquely the equilibrium state of a pure substance in two-phase state. The volume-based formulation of two-phase equilibrium in terms of the volume function coefficients has been derived for the Peng-Robinson

Table 8. Binary Interaction Coefficients for the Reservoir Fluid Used in Example 4

Component	N ₂	CO ₂	C ₁	PC ₁	PC ₂	PC ₃	C ₁₂₊
N ₂	0.000	0.000	0.100	0.100	0.100	0.100	0.100
CO ₂	0.000	0.000	0.150	0.150	0.150	0.150	0.150
C ₁	0.100	0.150	0.000	0.035	0.040	0.049	0.069
PC ₁	0.100	0.150	0.035	0.000	0.000	0.000	0.000
PC ₂	0.100	0.150	0.040	0.000	0.000	0.000	0.000
PC ₃	0.100	0.150	0.049	0.000	0.000	0.000	0.000
C ₁₂₊	0.100	0.150	0.069	0.000	0.000	0.000	0.000

Table 9. Overall Properties of the Mixture of the Reservoir Fluid from Table 7 (50% of volume) with N₂ at the Initial Pressure $P_{\text{ini}} = 30.34$ MPa and Resulting Phase Properties in Two-Phase Flash at Constant Temperature $T = 413.71$ K and Volume (Example 4)

Property	Unit	Overall mixture	Phase 1	Phase 2	K_i -values
Molar concentration	mol m ⁻³	8386.44	6877.62	8863.05	
N ₂ mole fraction	–	0.466905	0.243471	0.521675	2.14266
CO ₂ mole fraction	–	0.007466	0.006159	0.007786	1.26421
C ₁ mole fraction	–	0.300435	0.210766	0.322416	1.52973
PC ₁ mole fraction	–	0.105051	0.130065	0.098920	0.76054
PC ₂ mole fraction	–	0.041061	0.084767	0.030347	0.35801
PC ₃ mole fraction	–	0.045060	0.158289	0.017305	0.10932
C ₁₂₊ mole fraction	–	0.034021	0.166484	0.001551	0.00932
Phase volume fraction	–		0.240057	0.759942	

The final pressure is $P = 32.66$ MPa.

Table 10. Overall Properties of the Mixture of the Reservoir Fluid from Table 7 (50% of volume) with CO₂ at the Initial Pressure $P_{\text{ini}} = 30.34$ MPa and Resulting Phase Properties in Two-Phase Flash at Constant Temperature $T = 413.71$ K and Volume (Example 4)

Property	Unit	Overall mixture	Phase 1	Phase 2	K_i -values
Molar concentration	mol m ⁻³	10211.55	9168.51	10335.60	
N ₂ mole fraction	–	0.000131	0.000103	0.000134	1.303750
CO ₂ mole fraction	–	0.568185	0.504174	0.574938	1.140360
C ₁ mole fraction	–	0.246739	0.214535	0.250136	1.165950
PC ₁ mole fraction	–	0.086275	0.091552	0.085719	0.936288
PC ₂ mole fraction	–	0.033722	0.043366	0.032704	0.754150
PC ₃ mole fraction	–	0.037006	0.063680	0.034192	0.536942
C ₁₂₊ mole fraction	–	0.027941	0.082591	0.022175	0.268497
Phase volume fraction	–		0.106291	0.893709	

The final pressure is $P = 31.27$ MPa.

equation of state, but the same concept can be used for other pressure-explicit equations of state as well.

We proposed a numerical algorithm for computation of the phase-split properties, which is based on a combination of the fixed point outer iteration and Newton's method in the inner iteration. To show efficiency of this approach we have performed results of numerical computations of multicomponent mixtures of different complexity. The results indicate that to achieve the same accuracy, the number of iterations of the VT-flash method based on the fixed point iteration is about the same as when using the PT-flash under the same physical conditions. As the final pressure is not known a priori when the volume is constant, the computation of VT-flash using the PT-flash combined with outer iterations, as suggested Refs. 6 and in 7, is necessarily inefficient. Our method provides the correct solution in practically the same number of iterations as one run of the PT-flash at the final pressure.

Acknowledgments

The work was supported by the member companies of the Reservoir Engineering Research Institute, and by the project Mathematical Modelling of Multi-Phase Porous Media Flow 201/08/P567 of the Czech Science Foundation.

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Appendix: Volume Function Coefficient for Peng-Robinson Equation of State

In this work, we use the Peng-Robinson equation of state⁹ in the form

$$P(V, T, n_1, \dots, n_c) = \frac{nRT}{V - B} - \frac{A}{V^2 + 2BV - B^2},$$

where R is the universal gas constant, $n = \sum_{i=1}^c n_i$ is the total number of moles, and coefficients A and B are given by

$$A = \sum_{i=1}^c \sum_{j=1}^c n_i n_j a_{ij}, \quad B = \sum_{i=1}^c n_i b_i$$

$$a_{ij} = (1 - \delta_{ij}) \sqrt{a_i a_j}, \quad b_i = 0.0778 \frac{RT_{i,\text{crit}}}{P_{i,\text{crit}}}$$

$$a_i = 0.45724 \frac{R^2 T_{i,\text{crit}}^2}{P_{i,\text{crit}}} [1 + m_i (1 - \sqrt{T_r})]^2,$$

$$m_i = \begin{cases} 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2, & \text{for } \omega_i < 0.5, \\ 0.3796 + 1.485\omega_i - 0.1644\omega_i^2 + 0.01667\omega_i^3 & \text{for } \omega_i \geq 0.5. \end{cases}$$

In these equations, δ_{ij} denotes the binary interaction parameter between the components i and j , $T_{i,\text{crit}}$, $P_{i,\text{crit}}$, and ω_i are the

critical temperature, critical pressure, and acentric factor of the i -th component, respectively. The volume function coefficient for the Peng-Robinson equation of state can be found analytically using (9) as

$$\ln \Phi_i = \ln \frac{V - B}{V} - \frac{b_i n}{V - B} + \frac{Ab_i}{BRT} \frac{V}{V^2 + 2BV - B^2}$$

$$- \frac{1}{\sqrt{2}BRT} \left[\frac{Ab_i}{2B} - \sum_{j=1}^c n_j a_{ij} \right] \ln \left| \frac{V + (1 + \sqrt{2})B}{V + (1 - \sqrt{2})B} \right|.$$

Manuscript received Apr. 8, 2010, and revision received July 4, 2010.